Proceedings of the Fifth International Symposium on Advanced Nuclear Energy Research

— Neutrons as Microscopic Probes —

March 10—12, 1993, Joyo Geibun Center, Mito, Ibaraki, Japan

Organized and Sponsored by
Japan Atomic Energy Research Institute

in Cooperation with

ATOMIC ENERGY SOCIETY OF JAPAN
THE PHYSICAL SOCIETY OF JAPAN
THE JAPAN INSTITUTE OF METALS
THE CRYSTALLOGRAPHIC SOCIETY OF JAPAN
THE JAPAN SOCIETY OF APPLIED PHYSICS
THE SOCIETY OF POLYMER SCIENCE, JAPAN
JAERI-Mレポートは、日本原子力研究所が不定期に公刊している研究報告書です。
入手の間合わせは、日本原子力研究所技術情報部情報資料課（〒319-11茨城県那珂郡東海村）にて、お申しごきください。なお、このほかに財団法人原子力啓発会資料センター（〒319-11 茨城県那珂郡東海村日本原子力研究所内）で複写による実費振込をおこなっております。

JAERI-M reports are issued irregularly.
Inquiries about availability of the reports should be addressed to Information Division, Department of Technical Information, Japan Atomic Energy Research Institute, Tokaimura, Naka-gun, Ibaraki-ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1993
Published by JAERI, November 1993
Proceedings of the Fifth International Symposium on Advanced Nuclear Energy Research

—Neutrons as Microscopic Probes—

March 10~12, 1993, Joyo Geibun Center, Mito, Ibaraki, Japan

Organized and Sponsored by
Japan Atomic Energy Research Institute

in Cooperation with
ATOMIC ENERGY SOCIETY OF JAPAN
THE PHYSICAL SOCIETY OF JAPAN
THE JAPAN INSTITUTE OF METALS
THE CRYSTALLOGRAPHIC SOCIETY OF JAPAN
THE JAPAN SOCIETY OF APPLIED PHYSICS
THE SOCIETY OF POLYMER SCIENCE, JAPAN
Organizing Committee

Chairman: Takumi ASAOKA (JAERI)

Members of Committee:
T. Akabane (NIRIM) K. Asai (JAERI)
Y. Endoh (Tohoku Univ.) Y. Fujii (Univ. of Tokyo)
Y. Hamaguchi (Muroran Inst. of Tech.) T. Hiraoka (JAERI)
M. Izumi (JAERI) M. Izawa (JAIF)
K. Ishigure (Univ. of Tokyo) M. Ishii (JAERI)
K. Kaji (Kyoto Univ.) Y. Kaneko (JAERI)
K. Katsumata (RIKEN) W. Kawakami (JAERI)
S. Kikuta (Univ. of Tokyo) S. Komura (Hiroshima Univ.)
T. Kondoh (JAERI) S. Matsuura (JAERI)
G. Matsumoto (Prof. emeritus, Nagoya Univ., H. Nakahara (Tokyo Metropolitan Univ.)
Fujita Health Univ.) T. Noda (NRIM)
M. Saitoh (JAERI) E. Shirai (JAERI)
E. Tachikawa (JAERI) H. Takahashi (JAERI)
T. Tamazawa (JAERI) M. Utsuro (Kyoto Univ.)
Y. Yamada (Prof. emeritus, Osaka Univ.) Y. Yamaguchi (Tohoku Univ.)
H. Yamaoka (Kyoto Univ.) T. Yanagisawa (PNC)
N. Watanabe (KEK)

Secretary:
S. Funahashi (JAERI) T. Kodaira (JAERI)
Y. Mitadera (JAERI) T. Numata (JAERI)
T. Takahashi (JAERI)

Secretariat of the Symposium:
Eiji Shirai
Department of Research Reactor
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11, Japan
Phone 0292-82-5318
Fax 0292-82-5258

Editorial Working Group

Leader: H. Takahashi
Members of Working Group:
N. Hiramatsu, M. Hoshi, H. Tomimitsu, H. Shitomi,
H. Ichikawa, K. Okumura, K. Yekoo
Proceedings of the Fifth International Symposium
on
Advanced Nuclear Energy Research
— Neutrons as Microscopic Probes —
March 10-12, 1993, Joyo Geibun Center, Mito, Ibaraki, Japan
Editorial Working Group
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken
(Received October 25, 1993)

Records of the 5th International Symposium on Advanced Nuclear Energy Research, which focused on the subject of "Neutrons as Microscopic Probes", are contained in this issue. It consists of opening address, two keynote lectures, special invited talk, closing address, nineteen invited papers which were orally presented, 129 contributed papers which were presented on posters and a panel discussion. The oral presentations were organized in the following six sessions, (1) Development of solid state physics with neutron probes, (2) Complex structure study with neutron probes, (3) Fundamental physics research with neutron beam, (4) Non-scattering research with neutron probes, (5) Novel application of neutron beam and (6) Technical innovation of neutron beam experiment. The posters were also classified into the six fields.

Keywords: Neutron, Probe, Beam, Scattering, Non-scattering, Solid State Physics, Structure, Beam Experiment, Microscopic
第5回原子力先端研究国際シンポジウム
—微視的プローブとしての中性子利用、「中性子が拓く新世界」—
1993年3月10日～12日 群馬県富岡市 常陸国際センター
論文集

日本原子力研究所東海研究所
編集ワーキンググループ

（1993年10月25日受理）

第5回原子力先端研究国際シンポジウムが「微視的プローブとしての中性子利用、中性子が拓く新世界」のもとに、1993年3月10日～12日にわたって開催された。本シンポジウムの主な内容は、(1)中性子をプローブとした物性研究の発展、(2)中性子をプローブとした複雑な構造の研究、(3)中性子の関連した基礎物理研究、(4)中性子ビームの非散乱利用研究、(5)中性子ビームの新しい利用法、(6)中性子ビーム実験の新技術、であった。また、パネル討論では、「JRR-3 M の利用と次世代中性子源」が論じられた。

本論文集は、22編の招待講演論文、129編のポスタービアーラ発表論文、パネル討論のサマリー論文及び討論記録を集録したものである。
PREFACE

In order to promote nuclear energy research most efficiently, the Japan Atomic Energy Research Institute makes it a rule to hold the "International Symposium on Advanced Nuclear Energy Research" every year choosing a contemporary subject as the title of the symposium. In March 1993, the fifth symposium was held in Mito under the title "Neutrons as Microscopic Probes" to cope with the remarkable progress in the utilization of thermal and cold neutron beams made possible in Japan by the completion of JRR-3M in JAERI in 1990.

Neutrons have become one of the most powerful microscopic probes in condensed matter research in the six decades since their discovery. In the early days, neutron beams could be used only for solid state physics and other limited purposes, but now research with neutron beams has grown extensively to include chemistry, polymers, biology, surface science, engineering materials and practical applications as the main research fields. In the symposium, twenty-two invited lectures and a panel discussion were programmed to cover a wide range of topics including most of these fields and the future application of neutron beams as well as the future development of neutron sources. Up to 129 contributed papers were presented on the posters classified in the six sessions.

During the three days, about 400 people from 11 countries participated in the symposium. Through both the oral and poster presentations and the panel discussion and also through the enthusiastic discussions between the participants, it was made clear that research with neutrons is growing further in various fields extending from extremely advanced solid state physics to very practical applications with commercial uses. One of the issues often mentioned during the symposium was that utilization of pulsed neutrons generated with high energy accelerators increased the variety of the neutron research field widely and that the steady neutron beams from reactors and the pulsed beams are playing complementary roles. Complementarity of neutrons and photons was also discussed as an important matter in the symposium. It is recognized that not only more intense neutron sources but also more numerous beams are required. At the same time, numbers of future advanced neutron source plans in the world reported in the symposium offer a bright future toward the 21st century for research with neutrons as microscopic probes.

On behalf of the Japan Atomic Energy Research Institute, we wish to express our sincere thanks to all the persons who contributed to make the symposium most successful.

Eiji Shirai
Symposium Secretary
CONTENTS

Opening Address .................................................. 1
S.Shimomura (President, JAERI)

Keynote Lectures
I-1 Expectations for Neutrons as Microscopic Probes ............ 3
M.Date (Osaka Univ.)
I-2 Neutrons as a Probe – An Overview – .......................... 8
M.Iizumi (JAERI)

Special Invited Talk
I-3 Prospect for Neutron Probes in the 21st Century ............ 17
G.H.Lander (EITU, Germany)

Topical Invited Talk
I-4 Boron-Neutron Capture Therapy for Incurable Cancer and
Inoperable Brain Tumors ............................................ 25
H.Hatanaka (Teikyo Univ.)

Session I : Development of Solid State Physics with Neutron Probes
I-5 Phase Transitions and Neutron Scattering .................... 29
G.Shirane (BNL, USA)
I-6 Recent Development in Magnetic Neutron Scattering Studies .... 36
Y.Endoh (Tohoku Univ.)
I-7 Expanding the Frontiers of Neutron Scattering .............. 44
A.D.Taylor (RAL, UK)
I-8 Alloys Studied by Neutron Scattering .......................... 52
Y.Morii (JAERI)

A Short Note on Early Observations of Neutron Scattering by Crystals
R.R.Hashiguchi (Univ. of Tokyo Prof. of Emeritus) ......... 60

Session II : Complex Structure Study with Neutron Probes
I-9 Polymer Research by Neutron Scattering ..................... 63
D.Richter (KFA, Germany)
I-10 SANS Studies of Space-time Organization of Structure in Polymer Blends ........................................... 73
T.Hashimoto, H.Jinnai, H.Hasegawa (Kyoto Univ.)
C.C.Han (NIST, USA)
I-11 Neutron Diffraction on Random Systems ...................... 84
H.Ohno (JAERI)
I-12 Biology with Neutron Radiation ........................................... 92
G.Zaccaï (ILL, France)

Session II: Fundamental Physics Research with Neutron Beam

I-13 Fundamental Research with Neutron Interferometry ................. 97
H.Rauch (Austria Univ., Austria)

I-14 Expectations for Neutron Experiments
   – An Electron Physicist’s View – ..................................... 109
A.Tonomura (Hitachi Ltd.)

I-15 Fundamental Physics with Ultracold Neutrons ..................... 117
M.Utsuro (KURRI)

Session IV: Non-scattering Research with Neutron Probes

I-16 Neutron Radiography – Status and International Prospects ....... 125
J.P.Barton (NRE Inc., USA)

I-17 Uses of Reactor Neutrons for Studying the Microcomposition
   of Materials ....................................................................... 133
R.E.Jervis (Univ. of Toronto, Canada)

Session V: Novel Application of Neutron Beam

I-18 Commercial Applications of Neutron Scattering .................. 145
M.T.Hutchings (Harwell Lab., UK)

I-19 Complementary Applications of Scattering by Neutrons and SRX-rays
   ................................................................. 153
Y.Fujii (Univ. of Tokyo)

I-20 Neutron Reflectometry ...................................................... 161
A.D.Taylor, J.Penfold (RAL, UK)

Session VI: Technical Innovation of Neutron Beam Experiment

I-21 New Techniques in Neutron Scattering .............................. 163
J.B.Hayter (ORNL, USA)

I-22 Applications of Polarized Neutrons ................................ 171
F.Mezei (HMI, Germany)

Panel Discussion: Future Research with Neutrons
   – from JRR-3M to Next Generation Neutron Sources – ............ 179
   Chairman: Y.Yamada (Osaka Univ. Prof. Emeritus)

Summary Talk ........................................................................... 193
T.Fuketa (JAERI)

Authors Index
<table>
<thead>
<tr>
<th>Session I: Development of Solid State Physics with Neutron Probes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P-101</strong> Neutron Diffraction Study in AgCrO₃</td>
</tr>
<tr>
<td>Y.Oohara, H.Yoshizawa (Univ. of Tokyo)</td>
</tr>
<tr>
<td>S.Mitsuda (Science Univ. of Tokyo)</td>
</tr>
<tr>
<td>N.Yaguchi, H.Kuriyama, T.Asano, M.Mekata (Fukui Univ.)</td>
</tr>
<tr>
<td><strong>P-102</strong> Crystal Field Splitting in CeAs and CeP under High Pressure</td>
</tr>
<tr>
<td>Y.Oohara, Y.Okayama, H.Takahashi, H.Yoshizawa, N.Mori (Univ. of Tokyo)</td>
</tr>
<tr>
<td>S.Mitsuda (Science Univ. of Tokyo)</td>
</tr>
<tr>
<td>T.Osakabe, Y.Haga, M.Kohgi, T.Suzuki (Tohoku Univ.)</td>
</tr>
<tr>
<td><strong>P-103</strong> Lattice Instability of High-Tc Oxide Superconductors Studied by Inelastic Neutron Scattering</td>
</tr>
<tr>
<td>M.Arai (kobe Univ.)</td>
</tr>
<tr>
<td>K.Yamada, Y.Endoh, S.Hosoya (Tohoku Univ.)</td>
</tr>
<tr>
<td>Y.Hidaka (NIT)</td>
</tr>
<tr>
<td>A.C.Hannon, A.D.Taylor (RAL, UK)</td>
</tr>
<tr>
<td><strong>P-104</strong> Structural Phase Transitions of NaV₄O₁₁ and SrV₄O₁₁</td>
</tr>
<tr>
<td>Y.Kanke, F.Izumi, K.Kato (NIRIM)</td>
</tr>
<tr>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
<tr>
<td>E.Akiba (Natl. Chem. Lab. for Industry)</td>
</tr>
<tr>
<td><strong>P-105</strong> Neutron Scattering Study of Heisenberg-like Spin Glass Ni₃Mn₋₁₋₂TiO₅</td>
</tr>
<tr>
<td>H.Kawano, H.Yoshizawa (Univ. of Tokyo)</td>
</tr>
<tr>
<td>A.Ito (Ochanomizu Univ.)</td>
</tr>
<tr>
<td><strong>P-106</strong> Spin Dynamics of Concentrated Metallic Spin Glasses</td>
</tr>
<tr>
<td>K.Motoya, S.Kubota (Saitama Univ.)</td>
</tr>
<tr>
<td><strong>P-107</strong> On the 100 Magnetic Diffuse Peak in γ-Fe Precipitates in Cu</td>
</tr>
<tr>
<td>Y.Tsunoda (Osaka Univ.)</td>
</tr>
<tr>
<td>R.M.Nicklow (ORNL, USA)</td>
</tr>
<tr>
<td><strong>P-108</strong> Site Preference, Superconductivity and Magnetism in Pb₅Sr₂Y₁₋₃Ca(Cu₁₋ₓMₓ)₀ₓ(M=Fe,Co,Ni,Zn,Ga)</td>
</tr>
<tr>
<td>Y.Kolke, M.Kalwa, M.Kato, H.Sunagawa, T.Noji, Y.Saito, T.Kajitani, N.Kobayashi (Tohoku Univ.)</td>
</tr>
<tr>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
<tr>
<td><strong>P-109</strong> Crystal Structures of New Cuprates Containing CO₃ Analyzed by the Rietveld Method of Neutron Powder Diffraction</td>
</tr>
<tr>
<td>Y.Miyazaki, H.Yamane, T.Kajitani, K.Hiraga, T.Hirai (Tohoku Univ.)</td>
</tr>
<tr>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
</tbody>
</table>
P-110  Polarization Analysis on Two-dimensional Antiferromagnet ErFe$_2$O$_4$  
H.Kito, J.Akimitsu (Aoyama-Gakuin Univ.)
K.Siratori (Osaka Univ.)
M.Nishi (Univ. of Tokyo)  

P-111  Phonon Dispersion in Layered Structure ErFe$_2$O$_4$  
H.Kito, J.Akimitsu (Aoyama-Gakuin Univ.)
S.Funahashi (JAERI)
K.Siratori (Osaka Univ.)  

P-112  Crystal Structure and Superconductivity of LnBa$_3$Cu$_4$O$_{x}$  
(Ln=Ho,Er,Y,Dy and Gd) Superconductors  
T.Ishigaki, K.Mori, Y.Kawaguchi, Y.Hamaguchi (Muroran Inst. of Tech.)
S.Katano, S.Funahashi (JAERI)  

P-113  Neutron Scattering Study on the Spin Dynamics of the Two  
Dimensional Square Lattice Antiferromagnet, La$_3$NiO$_4$  
K.Nakajima, K.Yamada, S.Hosoya, Y.Endoh, T.Omata (Tohoku Univ.)
M.Arai (Kobe Univ.)
A.D.Taylor (RAL, UK)  

P-114  Polarized Neutron Scattering Study of $\delta$-Mn  
M.Shiga, H.Nakamura (Kyoto Univ.)
M.Nishi, K.Kakurai (Univ. of Tokyo)  

N.Yamada (Univ. of Electro-communications)
N.Takada, K.Kohn (Waseda Univ.)
S.Funahashi (JAERI)  

P-116  Neutron Scattering Experiments on Antiferromagnetic ABX$_3$ Systems:  
Study of the Haldane Conjecture  
K.Kakurai, T.Inami (Univ. of Tokyo)
K.Nakajima, S.Itoh (Tohoku Univ.)
H.Tanaka (Nagoya Univ.)
M.Enderle (Univ. of Mainz, Germany)
K.N.Clausen (RISO, Denmark)
M.Steiner (Hahn-Meitner-Institut, Germany)  

P-117  Crystal Structure Refinement of Alloys and Hydrides of Zr(Mn$_{1-x}$-M)$_2$  
with M=V,Fe,Co,Ni and Al  
S.Fujitani, I.Yonezu (Sanyo Electric Co. Ltd.)
D.Fruchart, J.L.Soubyroux, L.Pontonnier, S.Miraglia (CNRS, France)  

P-118  Neutron Depolarization Studies on Magnetic Flux in Superconductors  
T.Watanabe, K.Yamada, Y.Endoh, N.Toyota (Tohoku Univ.)
S.Itoh (KEK)
H.Kojima, I.Tanaka (Yamanashi Univ.)
<table>
<thead>
<tr>
<th>Page</th>
<th>Title</th>
<th>Authors</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-119</td>
<td>Magnetic Structure in Single Crystal of Antiferromagnetic Heavy Fermion Superconductor, UPd_{2}Al_{3}</td>
<td>H.Kita, A.Donni, Y.Endoh, N.Sato, T.Komatsubara (Tohoku Univ.) K.Kakurai (Univ. of Tokyo)</td>
<td></td>
</tr>
<tr>
<td>P-120</td>
<td>Neutron Scattering Study of UX_{4}(X=Ga,Ge)</td>
<td>Y.Kuroiwa, M.Kohgi, T.Osakabe, N.Sato (Tohoku Univ.) Y.Onuki (Univ. of Tsukuba)</td>
<td></td>
</tr>
<tr>
<td>P-121</td>
<td>Sample Dependence of Magnetic Ordering in the Ytterbium Monopnictides YbN and YbP</td>
<td>A.Donni, M.Kohgi, T.Suzuki (Tohoku Univ.) L.Keller, P.Fischer, A.Furrer (ETH Zurich, Switzerland)</td>
<td></td>
</tr>
<tr>
<td>P-122</td>
<td>Soft Modes and Phase Transition at 74K in Rb_{2}ZnCl_{4}</td>
<td>H.Mashiyama, K.Sugimoto (Yamaguchi Univ.) Y.Oohara, H.Yoshizawa (Univ. of Tokyo)</td>
<td></td>
</tr>
<tr>
<td>P-123</td>
<td>Structural Study in Metallic Sodium</td>
<td>H.Abe, K.Ohshima, T.Suzuki, S.Hoshino (Univ. of Tsukuba) K.Kakurai (Univ. of Tokyo)</td>
<td></td>
</tr>
<tr>
<td>P-124</td>
<td>Magnetic Ordering in Delafossite-type Rhombohedral Antiferromagnets</td>
<td>M.Mekata, Y.Ajiro, N.Yaguchi, H.Kuriyama, T.Asano (Fukui Univ.) H.Kadowaki, Y.Oohara, H.Yoshizawa (Univ. of Tokyo) S.Mitsuda (Science Univ. of Tokyo)</td>
<td></td>
</tr>
<tr>
<td>P-125</td>
<td>Universality Classes of Magnetic Phase Transitions in the Stacked Triangular Lattice Antiferromagnets, CsMnBr_{3} and CsMnI_{3}</td>
<td>Y.Ajiro (Fukui Univ.) H.Kadowaki (Univ. of Tokyo)</td>
<td></td>
</tr>
<tr>
<td>P-126</td>
<td>Magnetic Structure of Fe_{1.2}NbS_{3}</td>
<td>T.Suzuki (Univ. of Tsukuba) S.Ikeda (KEK) J.W.Richardson (ANL, USA) Y.Yamaguchi (Tohoku Univ.)</td>
<td></td>
</tr>
<tr>
<td>P-127</td>
<td>Synthesis, Structure and Electrical Properties of the Thallium Ruthenate Pyrochlores</td>
<td>R.Kanno (Kobe Univ.) J.Huang, A.W.Sleight (Oregon State Univ.)</td>
<td></td>
</tr>
</tbody>
</table>
P-129 Cu Ion Disordering in High Ionic Conductor Rb$_2$Cu$_4$I$_3$Cl$_{13}$
H.Kawaji, T.Atake (Tokyo Inst. of Tech.)
R.Kanno (Kobe Univ.)
P.Izumi (NIRIM)
O.Yamamoto (Mie Univ.)

P-130 Determination of Paramagnetic $\chi(q,\omega)$ for a Metallic Antiferromagnet Mn$_7$Pt by TOF Method
Y.Todate (Ochanomizu Univ.)
K.Tajima, A.Yazaki (Keio Univ.)
S.Tomiyoshi (Ehime Univ.)
H.Ikeda (KEK)

P-131 Maximum Entropy Method for Neutron Powder Diffraction Data
M.Sakata, T.Uno, M.Takata, M.Takagi (Nagoya Univ.)
S.Kumazawa (Science Univ. of Tokyo)
C.J.Howard (ANSTO, Australia)

P-132 Phase Effect in 3-fold and 6-fold Potentials of CH$_2$Group on Q-Dependence in Neutron Scattering
Y.Ozaki (Nagoya Inst. of Tech.)

P-133 Anharmonic Thermal Vibrations of Be Metal Found in the Mem Nuclear Density Map
M.Takata, M.Sakata (Nagoya Univ.)
P.K.Larsen, B.B.Iversen (Aarhus Univ., Denmark)
S.Kumazawa (Science Univ. of Tokyo)

P-134 Neutron Scattering Study of MnX$_2$ ($X$=Br,I)
T.Sato (Tokyo Inst. of Tech.)
H.Kadowaki (Univ. of Tokyo)

P-135 Pressure Dependence of the Antiferromagnetic Ordering Temperature of Face-Centered-Cubic Iron
A.Onodera, Y.Tsunoda, N.Kunitomi (Osaka Univ.)
O.A.Pringle, R.M.Nicklow, R.M.Moon (ORNL, USA)

P-136 Magnetic Order in the Competing Interaction State of Ternary Intermetallics DyMn$_3$Si$_3$ and DyMn$_5$Ge$_3$
M.Ohashi, H.Onodera, T.Ono, T.Andow, Y.Yamaguchi (Tohoku Univ.)
S.Funahashi (JAERI)
H.Kobayashi (Electrotechnical Lab.)

P-137 Magnetic Phase Transition of CaNiCl$_4$
K.Ubukata, M.Motokawa (Kobe Univ.)
T.Inami, K.Kakurai (Univ. of Tokyo)
P-138 Magnetic Phase Transition of CsCuCl₃ in Pulsed Magnetic Field
M.Mino, K.Ubukata, T.Bokui, M.Arai, M.Motokawa (Kobe Univ.)
H.Tanaka (Nagoya Univ.)

P-139 Dynamic Magnetic Response of a Gap-type Kondo Material CeNiSn
M.Kohgi, K.Ohoyma, T.Osakabe, M.Kasaya (Tohoku Univ.)
T.Takabatake, H.Fujii (Hiroshima Univ.)

P-140 Magnetic Phase Diagram of Oxygen Nonstoichiometric La₂NiO₄₋ₓ
T.Omata, K.Yamada, K.Nakajima, S.Hosoya, Y.Endoh (Tohoku Univ.)

P-141 Spin Wave Excitations in a Kondo Material CsCu₃
M.Kohgi, T.Osakabe (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI)
Y.Onuki (Univ. of Tsukuba)
H.Yoshizawa (Univ. of Tokyo)

P-142 Powder Neutron Diffraction Study on Pb₃Sr₂YC₁₀₂₋ₓO₉₋ₓ (δ = 0.0 and 1.67)
H.Fujishita (Kanazawa Univ.)
M.Sato (Nagoya Univ.)
Y.Morii, S.Funahashi (JAERI)

P-143 Magnetic Order in Ternary Compounds TbMn₂Ge₂ and TbMn₂Si₂
S.Purwanto, M.Ohashi, H.Onodera, H.Yamauchi, Y.Yamaguchi (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI)

P-144 Neutron Powder Diffraction Study on NdₓFe₁ₓN.H
with 0 ≤ x < 3.0 and 0 ≤ y < 1.0
T.Kajitani, H.Kato, Y.Nakagawa, K.Hiraga (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI)
T.Iriyama, K.Kobayashi (Asahi Chemical Industry Co. Ltd.)

P-145 Incoherent Neutron Scattering of Hydrogen Bond Compounds
I. Experiments at Steady Reactor
Y.Noda, T.Tamura (Chiba Univ.)
S.Ikeda (KEK)
Y.Yamada (Prof. of Emeritus, Osaka Univ.)

P-146 Structure of Martensitic Phase and Phonon Instability in Cu₄Zn₃₀
A.Konishi, Y.Kuroiwa, Y.Noda (Chiba Univ.)
K.Fuchizaki (Kyushu Univ.)
S.Funahashi, S.Katano (JAERI)
H.R.Child (ORNL, USA)
H.Chou (BNL, USA)
Y.Yamada (Prof. of Emeritus, Osaka Univ.)
S.C.Moss (Univ. of Houston, USA)
<table>
<thead>
<tr>
<th>Page</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-147</td>
<td>Magnetic Structure of Itinerant Electron Antiferromagnets Mn&lt;sub&gt;T&lt;/sub&gt;-T:S/ (T=Cr,Fe)</td>
<td>H.Miki, K.Ohoyama, Y.Yamaguchi (Tohoku Univ.) S.Funahashi (JAERI) S.Tomiyoshi (Ehime Univ.)</td>
</tr>
<tr>
<td>P-148</td>
<td>Crystal Field State and Magnetic Ordering of a Low Carrier System CeP under High Pressure and Magnetic Field</td>
<td>T.Osakabe, M.Kohgi, T.Suzuki, Y.Haga (Tohoku Univ.) N.Mori, H.Takahashi (Univ. of Tokyo) S.Ikeda (KEK)</td>
</tr>
<tr>
<td>P-150</td>
<td>[110]TA&lt;sub&gt;i&lt;/sub&gt; Phonon Dispersion Relations of BCC, B2 and Heusler Phases in AuCuZn&lt;sub&gt;n&lt;/sub&gt; Alloy</td>
<td>A.Nagasawa, R.Yamauchi (Nara Women's Univ.) T.Makita, Y.Morii, S.Funahashi (JAERI)</td>
</tr>
<tr>
<td>P-151</td>
<td>High Pressure Neutron Diffraction Studies of the Magnetic Structures of Tb,Ho and Er</td>
<td>S.Kawano (KURRI) N.Achiwa (Kyushu Univ.) A.Onodera (Osaka Univ.) Y.Nakai (Sizuoka Inst. of Sci. and Tech.) B.Lebec (Riso, Denmark)</td>
</tr>
<tr>
<td>P-152</td>
<td>Neutron Quasi-elastic Scattering Study of Magnetic Fluctuations in Yb Monopnictides</td>
<td>K.Ohoyama, M.Kohgi, T.Otomo, T.Osakabe, A.Oyamada, T.Suzuki (Tohoku Univ.)</td>
</tr>
<tr>
<td>P-153</td>
<td>Neutron Scattering Study of Ce&lt;sub&gt;a&lt;/sub&gt;Au&lt;sub&gt;b&lt;/sub&gt;Sb&lt;sub&gt;c&lt;/sub&gt;</td>
<td>M.Kasaya, K.Kato, M.Kohgi, T.Osakabe (Tohoku Univ.)</td>
</tr>
<tr>
<td>P-154</td>
<td>Phonon Dispersion Anomaly in the Premartensitic &lt;br&gt;β&lt;sub&gt;1&lt;/sub&gt;-Phase Au-Zn Alloys</td>
<td>T.Makita, Y.Morii, S.Funahashi, H.Obono (JAERI) A.Nagasawa (Nara Women's Univ.)</td>
</tr>
<tr>
<td>P-155</td>
<td>Structural Phase Transition and Superconductivity in La&lt;sub&gt;T&lt;/sub&gt;-Ba&lt;sub&gt;Cu&lt;/sub&gt;O&lt;sub&gt;c&lt;/sub&gt;</td>
<td>S.Katano, S.Funahashi (JAERI) J.A.Fernandez-Baca (ORNL, USA) N.Mori, C.Murayama, Y.Ueda (Univ. of Tokyo)</td>
</tr>
</tbody>
</table>

XII
P-156 Diffraction Study on the Nonstoichiometric $\alpha$-$U_2N_7$ Phase .............................................. 522
H.Sorizawa, K.Fukuda, Y.Ishii, S.Funahashi (JAERI)
M.Katsura (Osaka Univ.)

P-157 Cooling Process Dependence of Spin Structure in the Reentrant Spin Glass Fe$_{71.8}$Al$_{28.2}$ ............................................... 530
J.Suzuki (JAERI)
H.R.Child (ORNL, USA)
M.Arai (Kobe Univ.)
Y.Endoh (Tohoku Univ.)

P-158 Neutron Scattering Study on Lithium Oxide ................................................................. 531
Y.Ishii, Y.Morii, S.Funahashi, H.Ohno (JAERI)
R.M.Nicklow (ORNL, USA)

P-159 Refinement of Phonon Eigenvector Phases from Intensities of Neutron Inelastic Scattering in Si ..................................................... 532
J.Kulda (ILL, France)
D.Strauch (Univ. of Regensburg, Germany)
Y.Ishii (JAERI)

Session 2 : Complex Structure Study with Neutron Probes

P-201 Spinodal Decomposition in Fluid Mixtures ................................................................. 541
K.Kawasaki, T.Koga (Kyushu Univ.)

P-202 Small Angle Neutron Scattering Study on a Phase Separation in a 3-Component Microemulsion System .................................................. 547
H.Seto, E.Yokoi, S.Komura (Hiroshima Univ.)
D.Schwahn (KFA, Germany)
K.Mortensen (Riso, Denmark)
J.Suzuki, S.Funahashi (JAERI)
Y.Ito (Univ. of Tokyo)

P-203 Neutron Diffraction from Lead Germanate Glasses ....................................................... 555
N.Umesaki (Government Industrial Res. Inst.)
T.M.Brunier, A.C.Wright (Reading Univ., UK)
A.C.Hammon (RAL, UK)
R.N.Seinclair (Harwell Lab., UK)

P-204 Phase Formation of Physically Associating Polymer Blends ........................................ 563
F.Tanaka (Tokyo Univ. of Agriculture and Technology)

P-205 SANS Study of Polymer Chains in Confined Space ....................................................... 571
H.Hasegawa, H.Tanaka, T.Hashimoto (Kyoto Univ.)
C.C.Han (NIST, USA)
P-206 Microscopic View of the Volume Phase Transition on Weakly Charged Temperature Sensitive Polymer Gels
M.Shibayama (Kyoto Inst. of Tech.)
T.Tanaka (MIT, USA)
C.C.Han (NIST, USA) ................................. 578

P-207 Diffractometer for Neutron Crystallography in Biology
- Japanese Project - ................................. 586
N.Niimura (Tohoku Univ.)

P-208 Structure Study for the Complex of HU Protein and DNA ................................. 592
I.Tanaka, N.Niimura (Tohoku Univ.)
I.Tanaka (Hokkaido Univ.)
M.Kataoka, K.Mihara, F.Tokunaga (Osaka Univ.)
K.Mita (NIRS)

P-209 Small Angle Neutron Scattering Study of the Initial Stage of Lysozyme Crystallization Process ................................. 599
Y.Minezaki, I.Tanaka, N.Niimura (Tohoku Univ.)
M.Ataka, T.Katsura (Natl. Inst. of Bioscience and Human-technology)

P-210 Phase Transitions and Structures of Methylammonium Compounds ................................. 604
O.Yamamuro, N.Onoda - Yamamuro, T.Matsuo, H.Suga (Osaka Univ.)
T.Kamiyama, H.Asano (Univ. of Tsukuba)
R.M.Ibberson, W.I.F.David (RAL, UK)

P-211 Structure and Dynamics of Aqueous Electrolyte Solutions by Neutron Scattering ................................. 612
T.Yamaguchi, M.Yamaguchi, H.Wakita (Fukuoka Univ.)
T.Takamuku (TOTO Ltd.)

P-212 Ion Dynamics in Molten Molten Melkaltal Nitrates ................................. 620
T.Kamiyama, Y.Nakamura (Hokkaido Univ.)
K.Shibata, K.Suzuki (Tohoku Univ.)

P-213 Double Crystal Diffractometer Arrangement for Very Small Angle Neutron Scattering with PNO in JRR-3M ................................. 627
K.Aizawa, H.Tomimitsu (JAERI)

P-214 Phase Separation and Ordering Process in Al-Li Alloys Studied by Small Angle Neutron Scattering and Neutron Diffraction ................................. 635
M.Furusawa (KEK)
S.I.Fujikawa (Tohoku Univ.)
J.M.Tranquada (BNL, USA)

P-215 Is there any Correlation between the Intermolecular Structures around Main-group Metal Ion in Liquid and Crystalline States? ................................. 641
K.Ichikawa, Y.Kameda, S.Kotani (Hokkaido Univ.)

XIV
P-216 Small Angle Neutron Scattering Study of Silica Suspensions
Y.Kimura, M.Kawaguchi (Mei Univ.)
J.Suzuki, S.Funahashi (JAERI)
Y.Izumi (Yamagata Univ.)

P-217 Chain Conformations of ABA Triblock Copolymers in
Microphase-separated Structures for SANS
Y.Matsushita, M.Nomura, J.Watanabe, Y.Mogi, I.Noda (Nagoya Univ.)
C.C.Han (NIST, USA)

P-218 Chain Conformations of the Component Polymers and the Microphase
Separation Structures of Homopolymer/Block Copolymer Blends
N.Torikai, Y.Mogi, Y.Matsushita, I.Noda (Nagoya Univ.)
C.C.Han (NIST, USA)

P-219 Neutron Diffraction Studies of Molten Ti- and Bi-Se Alloys
T.Usuki, Y.Shirakawa, S.Tamaki (Niigata Univ.)
M.Inui, S.Takeda (Kyushu Univ.)
K.Sugiyama, Y.Waseda (Tohoku Univ.)

P-220 Neutron Diffraction of Molten Noble Metal Halides
Y.Shirakawa, T.Usuki, S.Tamaki (Niigata Univ.)
M.Inui, S.Takeda (Kyushu Univ.)
K.Sugiyama, Y.Waseda (Tohoku Univ.)

P-221 Vesicle Formation in the Block Copolymer/Homopolymer Mixture
Studied by Scattering Methods
S.Koizumi, H.Hasegawa, T.Hashimoto (Kyoto Univ.)
J.Suzuki (JAERI)

P-222 Inversion of the Phase Diagram in Polymer Blends
Studied by Small-angle Neutron Scattering
H.Jinnai, H.Hasegawa, T.Hashimoto (Kyoto Univ.)
C.C.Han (NIST, USA)

P-223 Small-angle Neutron Scattering Study of Amorphous Si-Ti-C-O Fibers
K.Suzuya (KEK)
T.Kamiyama, K.Suzuki (Tohoku Univ.)
Y.Ito (Univ. of Tokyo)
K.Okamura (Univ. of Osaka Pref.)

P-224 Small Angle Neutron Scattering Study of Phase Separation in PMMA/SAN
Y.Ohishi, A.Uemura, M.Minobe (Sumitomo Chem. Co.,Ltd.)
K.Fuchizaki, J.Suzuki, S.Funahashi (JAERI)

P-225 Low-energy Modes and Medium-Range Correlated Motions
in Pd,Gex Alloy Glass
K.Shibata, H.Mizuseki, K.Suzuki (Tohoku Univ.)
P-225 Crystallization of Fe_{18}(Cu,Nb)_{12}(Si,B)_{24} Amorphous Alloy
Studied by Small Angle Neutron Scattering .......................... 709
M.Ohnuma, Y.Usui, Y.Hamaguchi (Mucoran Inst. of Tech.)
J.Suzuki, S.Funahashi (JAERI)

Session 3: Fundamental Physics Research with Neutron Beam

P-301 Superthermal UCN-production at JAERI Analysis .................. 717
H.M.Shimizu (KEK)
T.Kawal (KURRI)
K.Sakai (Tohoku Univ.)

P-302 The Specular Reflection from Multilayer Mirrors to Construct
the Interferometer for Cold Neutrons .................................. 723
H.Funahashi (Kyoto Univ.)
K.Aizawa, H.Tomimitsu (JAERI)
T.Ebisawa, S.Tasaki (KURRI)
M.Hashimoto, T.Takahashi (Univ. of Tokyo)
Y.O.Takahara (Ibaraki Natl. College of Tech.)

P-303 UCN-VCN Facility and Experiments in Kyoto University Reactor .... 729
Y.Kawabata, K.Okumura, M.Utsuro (KURRI)

P-304 Neutron Optics Using Transverse Field Neutron Spin Echo Method .... 738
N.Achiwa, M.Hino, Y.Yamauch, H.Takakura (Kyushu Univ.)
S.Tasaki, T.Akiyoshi, T.Ebisawa (KURRI)

P-305 Research on Highly Excited States of Nucleus by Slow Neutrons .... 744
M.Ohkubo (JAERI)

P-306 PNO-Apparatus and Its Test Use for Neutron Interferometry .......... 752
H.Tomimitsu, K.Aizawa (JAERI)
Y.Hasegawa, S.Kikut (Univ. of Tokyo)

Session 4: Non-scattering Research with Neutron Probes

P-401 JRR-3M Neutron Radiography Facility ............................. 759
A.Tsuruno, M.Matsubayashi (JAERI)

P-402 Neutron Radiography Research Activities at KURRI ................ 766
S.Fujine, K.Yoneda, K.Kanda (KURRI)

P-403 Neutron Imaging of Mice and Rats in Vivo with JRR-3 TNRF .......... 775
G.Matsumoto, K.Ohara (Fujita Health Univ.)
K.Kato (Inazawa Municipal Hospital)

XVI
P-404 Quantitative Neutron Radiography Using Neutron Absorbing Honeycomb - Basic Research and Application - ................................. 780
M.Tamaki, M.Oda, K.Takahashi, K.Ohkubo, K.Tasaka (Nagoya Univ.)
A.Tsuruno, M.Matsubayashi (JAERI)

P-405 Visualization and Measurement of Fluid Phenomena Using Neutron Radiography Techniques ........................................ 788
K.Mishima, T.Hibiki, S.Fujine, K.Yoneda, K.Kanda, H.Nishihara (KURRI)
A.Tsuruno, M.Matsubayashi, M.Sobajima, S.Ohtomo (JAERI)

P-406 Cold Neutron Radiography Using Low Power Accelerator .................................................. 796
Y.Kiyanagi, H.Iwasa (Hokkaido Univ.)

P-407 Application of Neutron Radiography to Flow Visualization .............................................. 802
N.Takenaka, T.Fujii, A.Ono (Kobe Univ.)
T.Nakazawa (Kobe Univ. of Mercantile Marine)
A.Tsuruno (JAERI)

P-408 Classification of Japanese Granitic Rocks and Clays by K,Ca,Rb,Sr and its Application to Archaeology .................................................. 810
T.Mitsuji (Nara Univ. of Education)

Y.Minai, Y.Ito, T.Tominaga (Univ. of Tokyo)
C.Yonezawa, M.Hoshi (JAERI)

P-410 Reactor Neutron-induced Prompt Gamma-ray Analysis and Instrumental Neutron Activation Analysis of Ancient Glassware .......................... 826
T.Tomizawa (Keio Univ.)
C.Yonezawa, M.Hoshi (JAERI)
Y.Minai, Y.Ito, T.Tominaga (Univ. of Tokyo)

P-411 Application of Neutron Radiography to Plant Research and Water Hydrology in Soil ............................. 834
T.M.Nakanishi, S.Matsumoto, H.Matsumoto, A.Yasunishi (Univ. of Tokyo)
H.Kobayashi (Rikkyo Univ.)
A.Tsuruno (JAERI)

P-412 The Cadmium Content in Bone of Osteoporotic Patients .................................................. 841
M.Terao, K.Iizuka (Otsuma Women’s Univ.)
M.Eguchi (Kanto Rosai Hospital)

P-413 High Quality Neutron Radiography Imaging Using Cooled CCD Camera - Tomography - .......................... 846
H.Kobayashi (Rikkyo Univ.)
P-414  Prompt Gamma-ray Analysis Using JRR-3M Cold and Thermal Neutron Guide Beams ........................................ 854
C.Yonezawa, A.K.Hajiwood, M.Magara, M.Hoshi, E.Tachikawa (JAERI)
H.Sawahata, Y.Ito (Univ. of Tokyo)

Session 5: Novel Application of Neutron Beam

P-501  Utilization of Thymine Analogue as a Boron Carrier for Neutron Capture Therapy ........................................ 863
Z.H.Zhang, Y.Oda, M.Takagaki, H.Kikuchi (Kyoto Univ.)
T.Kobayashi, K.Kanda, K.Ono (KURRI)

P-502  Electron-Ion Correlation in Liquid Te II ........................................ 870
S.Takeda, M.Inui (Kyushu Univ.)
S.Tamaki, K.Maruyama (Niigata Univ.)
Y.Waseda (Tohoku Univ.)

P-503  Gadolinium Neutron Capture Therapy: Preclinical Studies ........................................ 878
Y.Akine, N.Tokita, K.Tokuyose, M.Sato, H.Churei
(The Natl. Cancer Center Hospital)

P-504  Growth Inhibition of Human Pancreatic Cancer Grafts in Nude Mice by Boron Neutron Capture Therapy ........................................ 886
H.Yanagie, Y.Fujii, K.Kosaki, Y.Saegusa, T.Tomita, M.Sekiguchi (Univ. of Tokyo)
H.Kobayashi (Rikkyo Univ.)

P-505  Phantom Experiment of Depth-dose Distributions for Gadolinium Neutron Capture Therapy ........................................ 892
T.Matsumoto, K.Kato, Y.Sakuma (Musashi Inst. of Tech.)
A.Tsununo, M.Matsubayashi (JAERI)

P-506  Prompt Gamma-ray Spectrometry for Measurement of B-10 Concentration in Brain Tissue and Blood — Clinical Use and Experimental Study — ........................................ 899
Y.Nakagawa, K.Kitamura (Natl. Kagawa Children’s Hospital)
T.Kobayashi (KURRI)
K.Matsumoto (Tokushima Univ.)
H.Hatanaka (Teikyo Univ.)

P-507  Boron Neutron Capture Therapy for Children with Malignant Brain Tumor ........................................ 907
Y.Nakagawa, H.Komatsu, T.Kageji (Natl. Kagawa Children’s Hospital)
P.Tsuii (Natl. Okayama Hospital)
K.Matsumoto, K.Kitamura (Tokushima Univ.)
H.Hatanaka, T.Minobe (Teikyo Univ.)

P-508  Structure Analysis of K$_2$H(SO$_4$)$_2$ by Neutron Powder Diffraction ........................................ 915
S.Murakami, Y.Kuroiwa, Y.Noda (Chiba Univ.)
Y.Nakai, T.Kamiyama, H.Asano (Univ. of Tsukuba)
P-509 Study of Neutron Medical Irradiation Facility with Supermirror Neutron Guide Tube in JRR-3M
K.Soyama, M.Suzuki, H.Ichikawa (JAERI)
Y.Kawabori (KURRI)

P-510 Progress in Study of a Medical Reactor for Boron Neutron Capture Therapy
M.Sasaki, J.Hirota (MAPI)
S.Tamao (MHI)
K.Kanda (KURRI)
Y.Mishima (MISHIMA Inst. for Dermatological Res.)

P-511 Neutron Diffraction Topographic Observation of Ni-base Superalloy Single Crystals
H.Tomimitsu, K.Alzawa (JAERI)
K.Iijima, A.Yoshinari (Hitachi Ltd.)

P-512 Diffraction Plane Dependency of Elastic Constants in Ferritic Steel in Neutron Stress Measurement
M.Hayashi, M.Ishiwata (Hitachi Ltd.)
N.Minakawa, S.Funahashi (JAERI)

P-513 X-ray Residual Stress Measurement and Its Variation during Plane Bending Fatigue and Sliding Wear Processes in TiC,TiN,TiB2 and Al2O3 Coated Carbon Steels
T.Endoh, K.Idemitsu, M.Kawakami (Tokai Univ.)

Session 6: Technical Innovation of Neutron Beam Experiment

P-601 Application of Neutron Spin Echo Spectroscopy to Dynamical Behaviors of Condensed Matter
S.Komura, T.Takeda, H.Seto (Hiroshima Univ.)

P-602 Neutron Spin Echo Spectrometer at JRR-3M
T.Takeda, S.Komura, H.Seto, M.Nagai, H.Kobayashi, E.Yokoi (Hiroshima Univ.)
T.Ebisawa, S.Tasaki (KURRI)

P-603 Practical Conditions in the Neutron Diffraction under High Pressure
K.Kamigaki, M.Ohashi (Tohoku Univ.)

P-604 Neutron Scattering Cross Sections of Liquid Hydrogen and Deuterium for Cold Neutron Production
N.Morishima, D.Mizobuchi (Kyoto Univ.)

P-605 High Pressure Apparatus for Neutron Diffraction Study
G.Oomi (Kumamoto Univ.)
Y.Shiozaki (Hokkaido Univ.)
P-606 Polarized Thermal Neutron Field around Polarized Helium-3 Gas Cells in a Nuclear Reactor .............................. 989
K.Ishikawa, T.Iguchi, M.Nakazawa (Univ. of Tokyo)

P-607 Thermo-lumino Detector for a Neutron Diffraction ...................... 997
M.Hidaka, T.Morisako (Kyushu Univ.)
M.Nishi (Univ. of Tokyo)

P-608 Development of Neutron Optical Devices in JRR-3M ..................... 1004
K.Soyama, M.Suzuki, H.Ichikawa, T.Kodaira (JAERI)
Y.Kawahata (KURRI)

P-609 Neutron Measurements as Fusion Plasma Diagnostics .................. 1009
T.Nishitani (JAERI)
M.Hoek (JAERI, STA Fellow)

P-610 Current Status and Future of Utilization in Research Reactors ........ 1017
Y.Koyama, Y.Hoshi, D.Nemoto, H.Takahashi (JAERI)

P-611 Neutron Scattering Facilities for the Proposed New Research Reactor 1025
J.Boldeman, D.Cookson, R.L.Davis, M.M.Elcombe, C.J.Howard,
S.J.Kennedy, R.Knott, S.L.Town (ANSTO, Australia)

Authors Index ................................................................. 1027
Opening Address

Shozo SHIMOMURA
President
Japan Atomic Energy Research Institute

Good morning ladies and gentlemen. On behalf of the Japan Atomic Energy Research Institute which is going to hold the Fifth International Symposium on Advanced Nuclear Energy Research for three days with title of "Neutrons as Microscopic Probes", I would like to say a few words of greeting to those guests from abroad as well as to the participants who come from throughout Japan.

Our institute was established in 1956 for the purpose of the peaceful utilization of atomic energy. Since that time, we have continuously made our utmost efforts for the realization of our aim while the social demands for nuclear energy have seen much changes along with the times. Among them it is one of our most important and unchanged missions to make efficient use of "Neutrons as Microscopic Probes" as taken up as the title of the symposium and to open up a new world of science with neutrons since our institute possesses research reactors which are powerful neutron sources. As a matter of fact, we commenced operation of JRR-1 in 1957, and along with that, we commenced the activation analysis. Furthermore, in 1962, we commenced experimentation on neutron diffraction as soon as JRR-2 was completed. Since that time we have promoted the neutron utilization constantly. Scientists from universities have also utilized research reactors at our institute most effectively and have realized many many good results.

When we look at the utilization of "Neutrons as Microscopic Probes" in the world, we notice that neutrons were discovered in 1932 exactly thirty years prior to the completion of our JRR-2. Soon after that time, it was proven that neutrons diffract, and it became clear that they could be an important means for materials research. However, it was after World War II when neutrons generated in nuclear reactors became numerous enough to be used for peaceful purposes, that we actually began to use "Neutrons as Microscopic Probes".

The progress made in this area of research was dramatic after the War. In the 1950's to the 1960's, research reactors in the 10 to 25 MW class were constructed in many countries. Consequently much progress was made in solid state physics mostly with neutron diffraction and also with neutron inelastic scattering. In particular, it should be mentioned that knowledge on magnetic structure was enormously expanded through neutron diffraction in that period of time.

In the 1970's, high flux reactors became operational at the Oak Ridge National Laboratory and at the Brookhaven National Laboratory in the United States, as well as
at the Institut Max von Laue - Paul Langevin in Europe. The research developed greatly with their intense beams. The research area was widened to cover objects in the fields of polymers, biology, chemistry and so forth.

In the 1980's, pulsed neutrons became available for practical utilization since they are generated by spallation of nuclei with accelerators developed for high energy physics. In the past, the research reactors were the only practical neutron sources. We have seen advances into broader areas with the utilization of pulsed neutrons based on the time-of-flight measurement techniques.

In late 1980's, the importance of neutrons in the solid state physics was strongly recognized again when the high temperature superconductors was discovered. But at the same time, it was during that period that the high flux reactors were suspended for certain periods of time for various reasons.

In 1990, our institute completed the JRR-3M construction, which had been going on for five years. This research reactor was originally completed in 1964 as the first national reactor. At the reconstruction, it was modified to reinforce the neutron flux greatly and a cold neutron source and neutron guides were added, so that the total performance went up by leaps and bounds. Compared to the original reactor, the proportion of neutron beams was increased among the various uses to which the reactor was put, so that it can be said that JRR-3M was made to provide abundant "Neutrons as Microscopic Probes" as taken up as the title of this symposium. And fortunately, research in this area in Japan is growing more and more active at the moment.

Along with the neutron beams from reactors, we see steady development and utilization of pulsed neutrons from accelerators, and each has shown their superior characteristic qualities. In the 1990's, the research with "Neutrons as Microscopic Probes" is further growing to cover not only solid state physics but also more varied areas. As we head towards the 21st century, there are plans for higher neutron sources, and the new world opened up by neutrons will be affecting almost all areas of science and technology.

We have chosen this theme at this time, and have invited distinguished researchers from all over the world and Japan, and we are going to hear valuable presentations and see active discussions on these valuable research sources, i.e. neutrons. If we can contribute to the development of science, it would indeed be quite meaningful.

I would like to express my sincere gratitude to those of you who have taken time out of your busy schedule to participate in this Symposium. I pray that the Symposium will end in great success. Thank you very much.
EXPECTATIONS FOR NEUTRONS AS MICROSCOPIC PROBES

M. DATE

Department of Physics, Faculty of Science, Osaka University
Machikaneyama 1-1, Toyonaka, Osaka, 560 JAPAN

ABSTRACT

Neutrons have been used as microscopic probes to study structural and dynamical properties of various materials. In this paper I shall give a comparative study of the neutron research in the condensed matter physics with other typical microscopic methods such as X-rays, laser optics, magnetic resonances, Mössbauer effect and μSR. It is emphasized that the neutron study will extensively be important in future beyond the condensed matter physics. Chemistry, biology, earth sciences, material engineering and medical sciences will become new frontiers for neutron study.

INTRODUCTION

There is an increasing interest in applying neutron diffraction to various materials beyond the condensed matter problems such as chemistry and biology. Historically speaking, the main users for the neutron diffraction were condensed matter physicists who were willing to have structural informations of various crystals or spin configurations of magnetic materials. Soon after the first stage, it was found that the inelastic scattering phenomena provide fruitful information about the elementary excitations in solid, for example, phonons and magnons. The success in the inelastic scattering means that neutron is effective not only in determining the structures but also the microscopic properties of materials and many large facilities of the neutron diffraction study have been constructed. BNL in United States and ILL in France have been ranked as the central laboratories with high neutron flux machines providing various important and influential discoveries. The high flux is necessary because the inelastic scattering corresponds to the Raman scattering in optics and the scattering intensity is weaker than the Bragg scattering.

Japanese researchers have been suffering from lack of the high flux neutron source and they have been forced to visit foreign laboratories to extend their work for many years. Recently, however, the new facilities associated with JRR-3M in JAERI, Tokai have been constructed with nearly equivalent effectiveness with those in BNL and ILL. They consist of an epoch-making machines in Japan and large contribution is expected to all of the applicable branches of basic sciences for both the domestic and international users.
In this occasion, it seems to me most important to note that the neutron diffraction is extremely effective not only for the condensed matter physics but also for other basic sciences, chemistry, biology, earth and space material sciences and even for some industrial technologies. The present paper gives a perspective view of the role of the neutron diffraction technology with special concern to the comparative study with other microscopic tools in basic sciences. The comparison may clarify the objective status of the neutron diffraction and will lead the most efficient use of the new facility in JAERI in coming glorious days.

**COMPARATIVE STUDY OF MICROSCOPIC PROBES**

There are may ways to have informations in material science and they are classified into two groups. The traditional methods are macroscopic and the typical ways are mechanical, thermal and electro-magnetic studies. The key words through these methods are classical and synthetic. On the other hand, however, several microscopic methods are found in the 20th Century with the key words of modern and analytic. These methods directly present various informations on the atomic, molecular and electronic states in materials and they are listed in Table-1.

**Table 1  Comparison of Microscopic Probes**

<table>
<thead>
<tr>
<th>Method</th>
<th>Characteristics</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-rays</td>
<td>Mainly Structure-Analysis</td>
<td>Application of SR</td>
</tr>
<tr>
<td>Neutron</td>
<td>Structure-Analysis and Excitation-Analysis</td>
<td>Steady and Pulse Sources</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Spin Probe</td>
<td>High Resolution and MRI</td>
</tr>
<tr>
<td>Mössbauer effect</td>
<td>Supplement of NMR h.f.s. Monitor</td>
<td>RI Science</td>
</tr>
<tr>
<td>μSR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Probe</td>
<td>High Resolution and Spin Wave</td>
</tr>
<tr>
<td>Resonant optics</td>
<td>Laser-Raman Hole Burning</td>
<td>Laser and SR Science</td>
</tr>
</tbody>
</table>

The X-ray diffraction was the first microscopic and powerful way for determining atomic arrangement established in the beginning of this century. The key words are Bragg scattering and reciprocal lattice. The related theory strongly promoted the periodicity-physics and the concept is extensively developed to the electronic band theory of solid because the scattering of de Broglie wave of electron is similarly applied in solid.

A weak point of the X-ray diffraction is in the scattering intensity decrease in light atoms, especially hydrogen atom because the intensity is nearly proportional to the number of
electrons. In other words, the intensity is too heavy for heavy atoms so that flat scattering intensity is not obtained. In the neutron diffraction, the scattering is not electromagnetic but nuclear scattering and the cross section does not depend on the electron number. We have enough scattering intensity from hydrogen atoms. Moreover, the magnetic scattering due to neutron spin moment enables us to see the magnetic moment distribution in materials. Considering these properties, complementary use of neutron diffraction with that of X-ray is quite desirable for the atomic structure analysis.

A new trend in the X-ray analysis is use of synchrotron radiation (SR) beams. It supplies well controlled high intensity X-rays and clear diffraction pattern is expected by instantaneous irradiation of the beams. Construction of big SR machines is now proceeding in the world.

A characteristic importance of the neutron diffraction is the inelastic scattering as is described in the introduction and the reason is schematically shown in Fig.1, where the dispersion relations of photon, neutron and electron are illustrated by the logarithmic scale.

![Diagram](image)

**Fig. 1** Dispersion relations of neutron, electron and photon and main excitation in the matter.
A circle in Fig.1 represents the area where phonons, magnons and various excitations in materials are expected. Fortunately, the neutron dispersion line crosses the circle. This means that the neutron is the best particle to see these excitations because the cross section to see the Raman effect i.e. the inelastic effect is large when the excitations are close to the dispersion curve. The dispersion curve of electron is also not so far from the circle but electron is a charged particle and the interaction with matter is too strong so that it is not an adequate test probe. The test probe should be cool from various interactions in matter. X-rays, a kind of photons, are also cool for material interactions but the dispersion curve is rather far from the circle. This is one of the reasons why neutron is indispensable tool for a microscopic probe.

Two important neutron sources are developed. One of them is the steady neutron source obtained from the nuclear reactor and another is the pulsed neutron source generated by high energy proton beam collision to a target. The steady source is effective for various precise diffractionometry while the pulse source is easy to cover wide momentum and energy regions and both sources have been considered to be complementary. A new pulsed source complementary to that of JRR-3M is highly needed now in Japan.

NMR, ESR and Mössbauer effect belong to another categories of the microscopic test probes. The common key word is spin and these technologies have been developed after the Second World War. It is noticed that the spin angular momentum can be regarded to be an additional dimension of particles. For example, electron in solid may be described by three-dimensional Schrödinger equation and another freedom of the spin dimension. The nuclear spin is described with similar angular momentum operator but the interaction with matter is very small compared to that of electron spin. The nuclear spin couples with matter through the hyperfine interaction, quadrupole interaction and magnetic dipole interactions and NMR or Mössbauer effect provides electronic information through these couplings. This is the reason why NMR and Mössbauer effect have been widely used not only in physics but also in chemistry and biology. The key words in NMR are spin-echo in physics and high resolution for chemistry while MRI, magnetic resonance imaging or NMR-CT, has become a major CT-scanner for medical use. Electron spin has an intermediate character as a test probe in materials because various interaction with matter is not so weak as in nuclei. Isolated unpaired electron spin in solid offers rich information in materials and has been regarded as a good test probe. In ferro- or antiferromagnetic materials, on the other hand, the spins play an important role on the properties of materials themselves. ESR is thus regarded as a unique microscopic method to have material informations.

Resonant optics in Table-1 is becoming important by rapid progress in laser techniques and SR machines. The resonant optics originally means the atomic and molecular spectra analysis in the beginning of this century. After the discovery of laser oscillation phenomena, however, the light source is highly improved and laser-Raman techniques have been developed widely. It is noted that the hole burning technology, which has been used in the NMR study, is now effective to identify the microscopic analysis of electronic process. Laser is also very effective to follow very fast observation of chemical reactions in time of $10^{-12} - 10^{-15}$ sec.

Use of the SR machine to optical spectroscopy is recently developing because VUV and soft X-ray can excite inner shell electrons. Deep electron excitation produces rich variety in the electronic process so that it is effective to determine the band structure of materials.
It should be added finally that there are many other ways of the microscopic analysis out of Table-1. In the surface science, for example, electron microscope, electron diffraction and STM, scanning tunneling electron microscopy, are important method in this field. The details are not given in this paper.

EXPECTED FRONTIERS FOR NEUTRONS

Methodological importance of the neutron diffraction is given in the previous section. The main aim of this section is what is the frontiers of the future neutron diffraction research. The use in the condensed matter physics will extend with much variety but the present paper wishes to give new possibility in chemistry and biology sciences. Application of X-rays in these field gives many epoch-making success for determining the structures of many key-materials such as DNA. The next step is to see the dynamical information of these materials. For example, it is still not clear that how DNA moves to reproduce genetic materials in cells. Proton motion and displacement may be decisive for the action so that neutron diffraction may give important information in future. Moreover, the neutron diffraction is very effective to see the energy transfer mechanism because the inelastic scattering related to the energy transfer in the chemical and biological reaction will be investigated by applying the neutron diffraction. In the field of NMR, the wide application to the biological systems is now discussed in U.S.A. When high magnetic field up to 80 Tesla is achieved, the macromolecular interactions such as the antigen-antibody interaction will be analyzed using high resolution NMR spectroscopy. Neutron diffraction in such a system will be fruitful in future because the expected informations in NMR and neutron diffraction are complementary.

Technical support to realize advanced research in the neutron diffraction study is also important. The central idea is the armament with extreme physical conditions, temperature, pressure and high magnetic field. Millikelvin cryostat with high pressure, high magnetic field is now necessary for standard neutron diffraction work. Recently high pulsed magnetic field above 50 Tesla is becoming available and these facilities will be very effective for future neutron diffractions.

Finally, it is emphasized that the international and interdisciplinary cooperation should be a key to success above new frontiers. Neutron diffraction physicist should be professional but should have wide mind to all of highly qualified physicist, chemist and biologist. The present symposium will offer a good chance to have the cooperation.
NEUTRONS AS A PROBE
- AN OVERVIEW -

Masashi IIZUMI
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai, Naka, Ibaraki 319-11 Japan

ABSTRACT

As an introduction to the symposium a brief overview will be given about the features of neutrons as a probe. First it will be pointed out that the utilization of neutrons as a probe for investigating the structural and dynamical properties of condensed matters is a benign gift eventuated from the release of atomic energy initiated by Enrico Fermi exactly half century ago. Features of neutrons as a probe are discussed in accordance with the four basic physical properties of neutrons as an elementary particle; (1) no electric charge (the interaction with matter is nuclear), (2) the mass of neutron is 1 amu, (3) spin is 1/2 and (4) neutrons have magnetic dipole moment. Overview will be given on the uniqueness of neutrons as a probe and on the variety in the way they are used in the wide research area from the pure science to the industrial applications.

INTRODUCTION

As a speaker of the keynote lectures I understand that it is my role to speak something about the research utilizing neutrons as a probe especially from the users' point of view. Unfortunately I am an "ex-user" and hence not appropriate to talk about the present status and the frontier of the neutron research.

In this sense I am not the qualified person to deliver the keynote lecture in the opening session of this symposium. However I think I can make good use of this half-layman's point of view to speak to the non-experts on how neutrons are useful and how they are used as a probe.

In this opening session a lot of non-experts are in presence and there are variety of experts from the different fields since this symposium covers a wide variety of research fields related to the utilization of neutrons as a probe. Some attendants are the experts on the neutron sources which provide neutrons for the probe-use.

Therefore I think it may be useful to give an overview for the non-experts leaving the most advanced topics to be delivered by the speakers of the sessions to follow. I hope I can
give you a general view or guide map, by which you can place the detailed talks you are going to hear in a unified framework.

**ATOMIC ENERGY AND NEUTRONS**

Before going into the main subject I would like to make a brief comment on the relationship between the neutron utilization and the development of the atomic energy.

As you are aware neutrons as a probe are an indispensable tool in the basic as well as applied sciences. Everyone will admit that without neutrons the basic science especially the condensed matter physics has not reached the present status. The point I would like to emphasize is that the science developed by neutrons is a benefit of the release of the atomic energy and the development of nuclear engineering.

Soon after neutrons were discovered by Chadwick in 1932, the possibility of utilizing neutrons in a way similar to the X-rays as a probe were pointed out because of the wave nature of the neutron as a quantum particle and a few pioneering works followed. However real use of neutrons as a probe had not been possible until the dawn of the atomic energy.

Enrico Fermi succeeded to demonstrate the self-sustaining chain reaction in December 1942, just half century ago. He carried out some measurements on the wave nature, interference and mirror reflection of neutrons just after he realized the chain reaction and plenty of neutrons became available. This was the beginning of the use of neutrons as a probe.

Since then the research reactors were built in Oak Ridge, Brookhaven and in Great Britain and France and thus the neutron research became in full bloom. In accordance with the development of the atomic energy higher and higher neutron beams became available and this has brought the science utilizing neutrons to the present status.

The atomic energy is primarily the release of the nuclear energy through nuclear fission reactions and the nuclear reactors are the device for energy production. However from another point of view they are the sources of neutrons and very intense one at that. Then we can use them as probes which are the issue in the present symposium and also to produce radio-isotopes.

Therefore the release of the atomic energy has not only given us humankind a new means of energy generation instead of usual chemical energies but also bestowed us intense sources of neutrons which we can utilize as probes to develop various fields of science.

**WHAT IS A PROBE ?**

I think you know what the probe is, but a brief mention will be due here as a step in my talk.

A probe is something to be introduced into a sample in order to investigate properties of the matter by its response to the probe. The probe introduced into the sample encounters the entities of matter and they are partly scattered, partly absorbed emitting secondary radiation, or partly penetrates without interaction. The way how the sample responds to the probe tells us the internal state of the matter.
There are various items we want to know about the state of matter. What items we are interested in decides what the suitable probe to be used is.

As Prof. Date mentioned earlier we have various kinds of probes in hands and there are a great variety in the ways the probes are used.

It may be useful to compare features of the probes with each other but here I am just going to emphasize the uniqueness of the neutrons as a probe without going into details of that kind of comparison.

The synchrotron radiation is the strongest rival of the neutrons since the applied fields are overlapping with each other. Fujii is going to talk about the comparison of both in this symposium.

FEATURES OF THE NEUTRONS AS PROBES

Basic physical properties of a neutron are
a) it has no electric charge and then the interaction with matters is nuclear,
b) its mass is about 1 atomic mass unit, i.e. almost equal to the hydrogen nucleus,
c) its spin is 1/2 and
d) it has magnetic moment.
In the followings we are going to see how these properties are useful as probes.

NEUTRONS AS A ZERO-CHARGE PROBE

First let's pay attention to the property that the neutron does not have electric charge and it is neutral. This means that neutrons do not interact with electrons in the matter. The interaction with matters is that with nuclei which are in the core of atoms. This is entirely different from the light or electrons as probes. The latter two probes interact with electrons comprising the outer shell of atoms.

Nuclear, not electromagnetic, interactions are favorable as probes in two respects. First the microscopic sensitivity to each atom does not have any systematic dependence on the atomic number. Secondly the macroscopic penetrability through matter is generally very good.

Let's compare neutrons with X-rays with respect to the visibility, namely the sensitivity of the probes when they encounter with the specific atoms. In case of X-rays atoms with larger number of electrons, that is, the heavier atoms, are more visible. On the contrary lighter atoms have less visibility; especially the hydrogen atoms are hardly visible in comparison with heavier atoms.

By contrast neutrons shows diverse visibility which changes unsystematically from one nuclide to another. The visibility of hydrogen is not bad, which is important as mentioned later. In some cases the scattering strength is negative. In case of hydrogen the normal hydrogen has negative and the deuterium has positive and fairly large scattering strength. This fact is important in the application for the biological systems.
negative and the deuterium has positive and fairly large scattering strength. This fact is important in the application for the biological systems.

The good visibility of light elements for neutrons gives rise to the precise determination of the positions of light elements such as hydrogen and oxygen in the crystal-structure determination by neutrons.

For example neutrons are quite important in determination of the oxygen atoms in the crystals of high-Tc superconducting oxides in which the deviation or vacancies of oxygen atoms are likely to play some essential roles in the appearance of the superconductivity. The crystal structures of the oxides were determined promptly after the discovery of each oxide by the high resolution powder neutron diffraction methods.

The sensitivity of neutrons for light atoms and the distinction between different isotopes are especially valuable in studying the biological systems.

Hydrogen is one of the constituent elements which are contained in biological molecules with large numbers and the precise knowledge of the positions of each atom in the three-dimensional structure is quite important in relation to the function of the molecules.

The importance of neutrons as a structural probe with high sensitivity for the light atoms is obvious in this regard. Moreover there is one more unique aspect of utilizing the neutrons as the structural probe for hydrogen atoms. This comes from the difference between normal hydrogen and deuterium in regard to the scattering nature: namely, hydrogen has small and negative scattering amplitude in contrast to the positive one with the normal size for deuterium. Substitution of hydrogen with deuterium, or light water with heavy water, changes the scattering of the biological molecules themselves or those molecules in contrast to the solvent, which can be used in a very ingenious way for studying the structures of biological molecules. The details will be shown in the paper by Zaccar in this symposium.

Neutrons, as a zero-charge particles, can penetrate deeply through materials under investigation. This property is very favorable in the nondestructive testing of industrial products by neutrons in comparison with that by the X-rays. This aspect will be emphasized by Hutchings in his paper on commercial applications of neutrons.

The high penetrability and the selective absorption of neutrons for respective elements are the keys in the neutron radiography and the prompt-gamma-ray analysis which are the aspects covered by Barton and Jervis, respectively in this symposium.

**PROBE AS A QUANTUM WAVE WITH MASS 1 AMU**

The second feature of neutrons as a probe is their mass with 1 amu.

According to the de Broglie relations a moving particles with momentum $p$ and energy $E$ has wave nature with the frequency $\nu$ and the wavelength $\lambda$ given by

$$\nu = \frac{E}{h}, \quad \lambda = \frac{h}{p}.$$

Neutrons, like electrons which show wave properties demonstrated by, e.g., electron microscope, have wave properties with the frequency-wavelength relationship quite different from that for electrons because of the different mass of the particles.
The wave properties are most evidently demonstrated by the interference effect: the wave, once split into two paths, interferes when it put together again. The interference of the light was demonstrated by, e.g., Michelson interferometer.

The neutron's version of the interferometer was invented by Rauch, who is going to tell us directly in this symposium on the recent advances made in this field. It is marvelous to know the quantum effect manifesting itself in our daily scale, not in the atomic scale.

The neutron interferometer is important in investigating the fundamental problems in the quantum physics. Tonomura is going to discuss the related problems in connection with his recent achievements by the electron holography.

One of the interference phenomena in the atomic scale is the neutron diffraction. Neutrons incident on condensed matters are scattered collectively as waves, that is, the scattered waves from atoms interfere with each other and give rise to a diffraction pattern. The analysis of the pattern gives an information on the arrangements of the scattering centers, that is, the structure of the condensed matters in the atomic scale.

It is essential to have the wave-probe with wavelength which is the same order of magnitude as the typical size of the structure under investigation. Thermal neutrons extracted from the research reactors or pulsed sources are quite favorable in this respect, since they have energy of about 0.025 eV which corresponds to the wavelength of about 0.18 nm. This turns out to be the same order of magnitude as the interatomic distances in condensed matters.

The neutron diffraction method is used very widely to investigate the structure of condensed matters. The uniqueness of neutrons is most remarkable when they are used to determine the light atom positions in the crystals or macromolecules. Neutrons are indispensable in determining the arrangements of magnetic atoms in the various kinds of magnetic materials. This is because of the strong interaction between neutrons and magnetic dipoles as described later.

Neutrons are also useful to study the disordered structures of the condensed matters. The most disordered structure is the liquids which is the subject discussed by Ohno in this symposium.

The small-angle scattering is suitable to investigate the structures one level higher than those of atomic scale, such as density fluctuation in alloys or biological structures. Since larger wavelength is favorable for this purpose, the cold neutrons extracted from the cold sources through neutron guide tubes are used for the small-angle neutron scattering. Availability of the long wavelength neutrons is one of the favorable points of neutrons as a structure probe.

Various examples of the small-angle scattering will be given by Zaccai on the application to the biological systems and by Hashimoto on the application to the polymers.

**NEUTRONS AS A PROBE TO SEE ATOMIC MOTIONS**

In addition to the feature as the structural probe in the atomic scale thermal neutrons have another important feature in exploring condensed matters. It is the possibility of measuring the energy change when neutrons interact with condensed matters.
The energy of neutrons extracted from the research reactors distributes around 0.025 eV which is almost the same as the energy of elementary excitations in condensed matters, such as lattice vibrations or spin waves.

Neutrons incident on a condensed matter can either give energy to or get energy from the vibrating atoms and we can measure the energy of neutrons after scattering which is different from the energy of incident neutrons. This type of scattering is called the inelastic scattering by which we can get information about the excited states in the condensed matter. This gives us a detailed knowledge on the dynamics of condensed matters at the atomic level.

The feature of neutrons as a dynamic probe does not merely lie on the possibility of measuring the energy change upon scattering. The combination of the two features that the wavelength of neutrons is comparable with the size characterizing the structure of condensed matter in the atomic scale and that the energy of neutrons is comparable with the energy of thermal motions of the condensed matters in the atomic scale reveals nature of collective motions in the condensed matters. This is the most marvelous feature of neutrons as a microscopic probe.

Atoms in a condensed matter do not move individually but they move in a mutually connected way. This is a collective motion. It consists of waves propagating on the three-dimensional array of atoms in various directions with various wavelength.

When a neutron is scattered inelastically by the condensed matter, it usually excites or deexcites one of the propagating waves. The neutron does not hit a single atom but interacts with an array of atoms as a whole and exchange energy by exciting or deexciting the propagating wave. This comes from the wave nature of neutrons. The neutron can excite or deexcite more than two propagating waves. But the chance is less and the scattering does not give useful information but forms just a background.

The propagating atomic motions are characterized by the wave vector $\mathbf{q}$ and frequency $\nu$. The wave vector is a vector pointing the direction of propagation of the wave and having the magnitude of the reciprocal of the wavelength. The wave vector is determined by the momentum conservation relation of the scattering and the frequency by the energy conservation relation of the scattering. Thus the inelastic scattering of neutrons exciting or deexciting a propagating wave determines the wave vector and frequency simultaneously. Different configurations of the scattering give different sets of wave vector and frequency.

Thus we can obtain full information of the wave-vector versus frequency relations, namely the dispersion relations, of the elementary excitations in the condensed matters, such as phonons or magnons. This is one of the most essential information to understand the dynamical nature of the condensed matters. The dispersion relations are only part of the more general dynamical characteristics of the condensed matters studied by the neutron scattering.

The phase transition phenomena is closely related to the dynamical nature of solids revealed by the neutron scattering. An instability of a certain type of collective motion, that is the decrease of its frequency as a function of a state variable such as temperature, gives rise to a phase transition. This aspect of the phase transition is extensively disclosed by the inelastic neutron scattering. Shirane, one of the pioneers in this field, will tell us the recent advance in this symposium and Mori is also going to tell us his results on the relationship between the
martensitic phase transitions in a certain type of alloys and the lattice-dynamics observed by the neutron scattering.

Some remarks on the accuracy of measuring the energy change will be due here. The energy resolution of common neutron spectrometers is of the order of 0.1 meV which is enough to measure the thermal vibration of atoms in condensed matters.

In order to observe the atomic dynamics with lower energy, such as the motion of polymer chains related to the viscoelasticity of the polymers or spin fluctuations in the very vicinity of the critical temperature, we are in need of far better energy resolution, say 1 μeV or lower. Recent advance of the neutron spectroscopic technology provides us an ultimate resolution in the range of 1 μeV to 1 neV.

Richter will tell us how the high energy resolution machines contribute to reveal the dynamics of polymer in very detail.

One of the methods to improve the energy resolution is to lower the incident energy of neutrons used as the dynamical probe. An extreme in this direction is the utilization of ultracold neutrons which is important not only to improve the energy resolution but also to broaden the application of neutrons as a probe as Utsuro will mention in this symposium.

NEUTRONS AS A PROBE WITH SPIN

The property that the neutrons have spin 1/2 makes the scattering dependent on the nuclear spin; the probability of scattering for neutrons with spin in parallel with the nuclear spin is different from the one for anti-parallel alignment. This property introduces the distinction between coherent and incoherent scatterings. The former causes interference among the scattering from all the scattering centers, e.g. nuclei, and the latter is just a superposition of the scattering from each center and forms just a background to the coherent scattering. Most of the abundant information on the structures and dynamics in the atomic scale mentioned thus far is obtained by the coherent scattering.

The nuclear-spin-dependence can be used to study the nuclear magnetism, namely the alignment of nuclear spins on solid state lattices at very low temperature.

NEUTRONS AS A PROBE WITH MAGNETIC MOMENT

Neutrons have a magnetic moment, which means that a neutron is a microscopic magnet. When an atom has a magnetic moment, that is, when the electrons of the atom leave unpaired spins, neutrons are scattered through the magnetic interaction between dipole moments of neutrons and atoms. The magnitude of the interaction is of the same order as the nuclear interaction between neutrons and nuclei.

This property makes the neutrons as a unique probe to investigate the magnetic properties of solids at the atomic level. All the descriptions in the sections "PROBES AS A QUANTUM WAVE WITH MASS 1 AMU" and "NEUTRONS AS A PROBE TO SEE ATOMIC MOTIONS" on the neutrons as a structural and dynamical probe can be applied to the magnetic
structure, that is, the three-dimensional alignment of microscopic magnetic moments, and the spin dynamics.

The neutron scattering method has been instrumental and indispensable in the development of magnetism in the latter half of 20th century. The recent advance in this field will be reviewed by Endoh in this symposium.

One of the especially useful way of using the neutron-magnets as a probe is to align the direction of their magnets. The neutron beam with aligned neutron-magnets is called the polarized neutron beam and very useful not only for the magnetic studies by making it possible to separate the magnetic scattering from the nuclear scattering but also for more general neutron scattering research by separating various components of scattering by analyzing the directions of neutron-magnets after scattering.

An innovative method of utilizing the polarized neutron beam to measure the energy change upon scattering very accurately was invented by Mezei who is one of the invited speakers of this symposium.

A neutron spin under magnetic field makes a precessional motion. The Mezei's method is to measure the number of precession during the time of flight for a certain distance instead of measuring neutron's energy itself. By inverting the direction of neutron-magnets just after the scattering he can ingeniously introduce the echo effect in which the broadening of the precession angle due to the energy broadening of the incident neutrons can be canceled out by traveling the same distance after the inversion of the direction of neutron-magnets. By this method one is able to get rid of the energy broadening entirely and to measure a very fine energy change as a change of the precession angle. Mezei will tell us directly recent progresses of the method and applications.

**CONCLUDING REMARKS**

We have seen how the basic physical properties of neutrons are used as the features of neutrons as a probe. I tried to emphasize the uniqueness and diversity of the utilization of neutron probe. The details of the various application of neutron probe will be discussed in this symposium by the leading experts of the respect field.

The application of neutrons as a probe is still expanding very rapidly. The future trends of the neutron research will be mentioned in the special invited talk by Lander.

Some of the problems I could not cover are measurement techniques and the source problems. As for the former point Haytor will mention some recent progress and for the latter Taylor is going to discuss advantage of the pulsed source and Lander will tell us prospect towards the 21st century. A panel discussion is going to be dedicated to the future of neutron research including the source problem.

I hope that this symposium is successful to reconfirm the importance of the neutrons as a probe and to exchange opinions on what should be done to develop further the neutron research towards the coming 21st century.
PROSPECTS FOR NEUTRON PROBES IN THE 21ST CENTURY

G. H. Lander

Commission of the European Communities, Joint Research Centre, Postfach 2340, D-7500 Karlsruhe, Federal Republic of Germany

ABSTRACT

In this paper I use the economic concepts of supply and demand to attempt to analyze the future prospects for neutron research. The most severe problem is one of supply of neutrons. The question is whether the demand will be sufficient to overcome the considerable political and financial problems associated with providing the supply. A different mode of operation may be necessary in neutron research, especially with reactor-based sources.

SUPPLY

Reactor sources

50 years ago in Dec. 1942 the first reactor went critical in the squash courts of the University of Chicago. It had been ten years since the discovery of the neutron, four since the discovery of fission. We rushed collectively into the nuclear age. The benefits of this discovery have been aptly demonstrated at this (and similar) meetings and I will not enumerate them here, nor dwell on the darker side of nuclear technology. I too have spent a quiet day in Hiroshima.

The 1950's and 1960's saw a rush of building reactors in many countries of the world (Fig. 1) Most neutrons produced today come from reactors that are at least 25 years old. I estimate that there are at least 35 such reactors in the world (there are 32 such local correspondents in Neutron News) of equal to or greater than 1 MW, and the total number of neutron instruments\(^1\) is ~ 250. Only three reactors, those at Saclay in France (the Orphée reactor in 1980), that at Trombay in India (DHRUVA in 1984), and that in Indonesia (in 1987), have been built in the last 20 years.

Reactors fall into three classes:

(1) Those that for a number of different reasons have now been shut down, or face such a threat; examples are the two reactors at Harwell, (UK), and those at Delft (Holland), McMaster (Canada), and the CENG reactor Siloë in Grenoble (France).

\(^1\) Invited paper given at the 5th Int. Symposium on Advanced Nuclear Energy Research, 10-12 March 1993, Mito, JAPAN

---
(2) Those that are financially stable but have not been able to finance an upgrade; examples are in Missouri (US), Lucas Heights (Australia), Studsvik (Sweden), and Chalk River (Canada), and, regrettably, the two high-flux reactors in the US at Oak Ridge and Brookhaven National Laboratories.

(3) those that have managed a major upgrade; examples are Hahn-Meitner Inst. in Berlin (Germany), Jülich (Germany), Risø (Denmark), NIST (Washington, US), and the JAERI JRR-3 reactor here in Japan.

![Assured vs Uncertain Reactors over Time](image)

**Fig 1** Number of research reactors achieving criticality. An upgrade in which the reactor power is doubled is counted as a new start. Taken from Ref. 1, Moon (1985)

Of those in categories (1) and (2) one can predict that only a few will outlast this century. Those in category (3) may well last for 20 more years, but another 30 years is doubtful. The new reactors, e.g. Orphée in Paris and the renewed high-flux reactor at the Institut Laue Langevin in Grenoble (France) might well last for another 30 years, especially if a major upgrades can be financed in some 10-15 years time.

What has happened to 'stop' this vital supply line of reactor neutrons? One answer is that there has been a saturation in medical isotope production, and 'other' uses of nuclear energy. An obvious point is the decline of nuclear energy in the same years — no nuclear power plant has been ordered in the US for the last 15 years, and the strong opposition, essentially worldwide, to nuclear reactors. Of course this has played a major role, but in the years before Chernobyl (1986) I do not think that it was necessarily enough. By a historical chance, the emergence of neutron scattering as a technique applicable across a wide domain of condensed matter science, and particularly 'soft matter', came just too late to overcome the growing public opposition to nuclear reactors. Thus, if the importance of the cold neutrons produced and used so effectively at the ILL in France (and elsewhere), could have occurred just 10 years earlier, it is my belief...
that a number of new reactors could have been built. In fact only the reactor in Indonesia has been turned on since Chernobyl.

The high-water mark of the influence of reactors and the ILL was 1984, two years before Chernobyl, (and one year before ISIS became operational) when the Seitz-Eastman committee in the US decided that the next neutron source for the US should be a super-ILL reactor called the Advanced Neutron Source — a huge project at the Oak Ridge National Laboratory that will cost in the neighborhood of US$3 billion, and which is scheduled for completion in the early part of the next century. A reactor source to replace HFIR and HFBR, both of which were built in the 1960's, has some obvious advantages. Nine years of study have now been completed without earth being turned. The ANS may be built. Unfortunately, the agency in charge of building the ANS, the US Dept. of Energy (USDOE) has so many problems, from nuclear waste to contamination at the Hanford and Rocky Flats, Colorado, plants, added to which is a shortage of funds for basic research.

In conclusion, the long-term (2020 time frame) supply from reactor sources looks relatively bleak. It is to be noted that this is not only because of the public opposition to such sources, but also to the great difficulty of increasing the flux levels (or brightness). In this respect see Fig. 2. After 30 years the flux levels of ILL and the proposed ANS differ by a factor of less than one order of magnitude. This is to be compared with photon sources that have increased by 3 orders of magnitude in brightness in the 1980's alone — even spallation sources have increased a factor of ~50 in flux since 1980.

![Graph](image)

Fig. 2 The growth in steady state and pulsed neutron sources in the last 50 years. There is frequently dispute as how to normalize these two kinds of sources with respect to each other, but within a subset the comparison is well defined. This curve was produced by Bob Brugger for a Physics Today article in 1968. It has been much used since.
Spallation Sources

It is sometimes forgotten that the best early sources of neutrons were the accelerators of Lawrence and Cockcroft. However, the yield from fission rapidly outperformed these sources (see Fig. 2) and it was not until the 1970's that a number of spallation sources were under construction - the most important being at Argonne, here in Japan at KEK, and in the UK at the Harwell Linac (now closed).

The success of the smaller spallation sources has been considerable — although not revolutionary in the sense that everything can be done at them that can be done at reactors. In particular research efforts at reactors with polarized neutrons and triple-axis spectroscopy have not been seriously challenged (yet) by spallation sources. Moreover, for isotope production, and many of the other aspects of neutron research, the spallation sources do not compete well with reactors as the average fluxes are considerably below those at reactors. Scattering experiments can, if well matched to the source characteristics, use the peak flux, and are thus not dependent on the average flux.

The first second-generation spallation source ISIS in the UK has pushed further the technology of these machines, and has allowed a better extrapolation into the future. The power of ISIS is 160 kW (200 µA at 800 MeV). The flux levels are a factor of 50 above the first machine here in Japan, KENS commissioned in 1980. I think it is safe to say that ISIS has shown the complementarity between a source of this size and a 10¹⁵ reactor such as ILL, and that a source 6 times greater than ISIS (i.e. a 1 MW spallation source) could do all that ILL can do. In particular, the success at ISIS of the cold-neutron instruments such as CRISP and IRIS have removed many of the doubts about the capabilities of the sources at this end of the neutron spectrum. (These successes were predictable from the work on the first reflectometer POSY at IPNS at Argonne, and on the small-angle scattering machine here in Japan at KENS)

The really exciting long-term future of the spallation sources is that they rest on a different technology (one more efficient than fission in terms of heat produced for 1 neutron produced) and rest on a technology that is expanding in the world. The growth curve for accelerator sources does not (yet) show any sign of saturating (Fig. 2), and theoretically can be pushed to a 5 MW source even with present-day accelerator technology. Such a source, called the European Spallation Source, has been proposed in Europe and I expect it to be operating by 2020. Space-charge limitations with proton currents start to be a serious problem at 5MW, but accelerator technology is an advancing field, and one can readily imagine a source of even greater power in the late 21st century.

There is also a strong case that can be made for constructing spallation sources at the ISIS level. The cost today for such a source certainly will exceed $300 M, and that is the major problem. A recent example is the AUSTRON project, in which a group of central-European countries, which do not have a very strong tradition in neutron scattering, have come together to propose a spallation neutron project in Austria. They estimate the cost of an ISIS-type source with 15 instruments to be about $300M, and the Austrian Government has agreed to pay 1/3. Although this price is probably a bit low, this does represent an important
new initiative in neutron research. The Kohn Committee in the US has also just strongly endorsed a spallation source at the 1 MW level.

Another kind of source — a continuous spallation source (SINQ) is under construction at the Paul-Scherrer Institut in Switzerland. In some senses this source can be thought of as replacing a reactor, and will have a flux of $2 \times 10^{14}$ n-cm$^{-2}$-s. Because currents up to 1.5 mA are anticipated, much important work is being done on targets and moderators. At the moment future options do not favour extending this technology, but it becomes attractive for isotope production and transmutation studies aimed at burning nuclear waste.

An accelerator-driven spallation source has the advantage over a reactor that all the pieces can be replaced over a relatively short time frame — so 'creeping' upgrades become a strong possibility for the 21st century. (In this respect I should like again to emphasize the pioneering nature of the operation here at JRR-3. The ILL, also, is breaking new ground by replacing the central part of its reactor. Cutting up and disposing of the old pieces is proceeding well — I’m happy to say. Perhaps this method will also be applicable to other reactors?)

Thus the supply situation for spallation sources is considerably more optimistic than it is for reactors.

**Improving Technology**

When the HFBR started operating at Brookhaven in 1966 there were 10 neutron detector elements — one for every instrument. Today at the ILL there are $\sim 10^4$ detector elements. One can extrapolate this to $\sim 10^7$ detector elements at a source such as the ESS. This is one example of the increase in technology that has occurred in 25 years. The most explosive expansion has been in our ability to handle information. In Abingdon last year at the ESS workshop we were told that computers are now cheaper than shielding. When I did my first 3-axis measurement the machine was controlled by paper tape; now I am typing this manuscript on a plane on a lap top. We are all aware of this revolution, and it will further change both neutron research as well as our lives.

Detectors too have made huge strides, although they are still bulky, have too long dead times, are too sensitive to gamma's, and have (relatively) poor spatial resolution. Much of this is not too serious because the optics of neutron beams is for the most part rather poor (compared to photons for example), and they are slow moving and massive particles.

Huge amounts of data are intimidating to all of us, and I was pleased that one of the recommendations at the ESS Workshop last year was to start a real effort to improve data visualization. We need more of this type of hybrid programming — an area that has made great strides in high-energy physics, for example.

But we should not assume that improvements will continue to come in the supply side of neutron technology unless we are provided to make the investment. And yet, because of the difficulty of increasing the source fluxes, as compared to photon sources for example, we must make these investments. Many of the innovations we see today in neutron scattering are associated with the ILL, but
that is only half the story. In fact, as the ILL staff will quickly tell you, the ILL has been the beneficiary of a great number of ideas that came from smaller centers. Peter Egelstaff (see *Neutron News*, Vol. 2, #1, 1991) has been a strong proponent of the local sources feeding their ideas into a main central source for full exploitation, and the success of the ILL stems in a large part from such an arrangement.

Even today some of the most imaginative experiments are taking place at the smaller sources. One thinks of guide and cold-neutron development at Munich, Rauch on interferometry at Vienna, Rekveldt on domain effects in magnetization at Delft, Riste on non-equilibrium experiments at Kjeller (Norway), Arrott on perfect crystals at Vancouver, the experiments on nuclear ordering at Risø, and earlier at the Melusine (now closed) reactor in Grenoble, Stuhrmann on polarized targets in biology at Geesthacht, work on ultra-cold neutrons here in Japan at Kyoto and at Rhode Island, and chopper development at Braunschweig in Germany. The list is not exhaustive. A similar situation has developed with pulsed sources. The first reflectometer was built at IPNS, also the first chopper spectrometer, but they have been much improved at the ISIS source.

History may, however, be an unreliable guide to the future unless we are careful. Many of the smaller centers are in financial difficulties and may be gone within the next 10 years. The ILL has, in the past, been able to maintain an investment budget of ~10%, but financial problems make it unlikely that this will be the case when it comes back on line in 1995. The US centers are particularly guilty of exploiting the past at the expense of the future, and have not been able to maintain enough instrument development — again because of financial pressure rather than management decisions. The developments at NIST are an encouraging reversal of this trend; see the articles by Mildner et al. on capillary guides, and Downing and Lamaze on neutron depth profiling.

Some idea of the state of instrument and technology development may be gathered from looking at the Proceedings of the Oxford Conference on Neutron Scattering in 1991, published in Physica B in 1992, which are 1072 pages long and contain 336 papers. Of these only 17 are on new techniques, i.e. 5%. Of these 17, eleven come from France and Germany, and only 1 (from NIST) from the USA. Although instrument developers go to other conferences as well, e.g. the SPIE Conference in California last year for detector development, this small number of instrumental papers at the major tri-annual neutron scattering meeting is cause for concern for the future. Let us hope that ILL can get back to a 10% investment budget, and other centers can reach this level of investment.

DEMAND

Fortunately the demand side of the equation is easy. We have seen a continuous increase in the usage of neutrons across an ever-widening range of materials. Before returning to scattering investigations, let me look at 'other' use of neutron beams. Many of these have been covered in this Conference; isotope production, the doping of Si, activation analysis, fuels testing, the production of muon beams, depth profiling, medical neutron irradiation, boron-capture therapy, radiography etc. I am not an expert in these, but one thing does strike me. With the exception of the production of transuranium isotopes, e.g. Cf, none of the above techniques really push for the highest fluxes. Radiography, for example, is more interested in portable sources, than in central high-flux ones.
Of course, they all depend on a supply of neutrons, but, unlike scattering, they do not normally want 'more'. This may mean a divergence in the future that may further weaken the overall demand for better neutron sources. For example, if boron-capture therapy would rather have a number of small reactors installed near hospitals, that group of researchers may not be interested in joining the lobby pushing for a high-flux source. The ANS has attempted to obtain wide-based support, but the interest in the transuranium isotopes is not, frankly, as high as they would wish. So this aspect of the demand side has to be treated with caution: a similar situation has emerged in the synchrotron community with lithography. Initially, IBM, for example, was very involved with the premier dedicated synchrotron, the NSLS at Brookhaven, but now has more interest in small table-top synchrotrons that they can change as they want. Lithography cannot be used as an argument for even brighter synchrotrons.

When we turn to scattering the trend is quite clear — positive. Many surveys have been performed in the last ten years; they all show a growth in users that is doubling in the 10-15 year period. The last authoritative survey by the Fowler Committee in Britain shows a rise from 250 users in 1975 to over 500 in 1988. Similar increases are present in all countries having access to high-flux sources. In 1990 (the last full year of ILL operation) 2400 separate visits were made by 1500 outside visitors to Grenoble, resulting in some 500 publications per year. This number is exceeded at user facilities only by the NSLS, Brookhaven.

I shall not enumerate all the diverse fields covered by scattering in this paper — the interested reader should just glance at the rest of the Proceedings. What has been remarkable has been the diversification that has taken place in the last 20 years. A glance at the ICNS Proceedings shows that the conventional fields of neutron scattering, magnetism, structure, and phase transitions, is still lively. In fact, with the advent of new materials such as heavy fermions, the high T systems, multilayers, and C\textsubscript{60}, the interest has even grown. Completely new fields on polymers (see the paper by Richter), biology (Zaccar), and industrial applications (Hutchings) are growing even faster. Given that 'neutron scattering is the single most revealing technique in condensed matter science' (a phrase that comes from the 60's — not a recent invention of proponents of high-flux sources!), all this development is not surprising to those of us who believe in neutrons.

All this body of work is, however, flux limited. For sample size, for spatial and energy resolution, unfortunate compromises are being made in every experiment.

CONCLUSIONS

Let me dare by ending with some recommendations (in addition to the one calling for 10% investment in techniques), as well as some predictions.

1) We should give more publicity to the use of neutrons and their benefits. Whether we like it or not today’s world is a capitalistic one and advertising is one of the basic tenets of our society. We need to organize conferences on the industrial use of neutrons — we need to find a way to get more industrial companies interested in neutrons. We need to keep encouraging people who use other techniques (synchrotrons, NMR, etc.) to think of neutrons as another alternative.
2) We need to find a better way to enumerate that we are doing 'small science' at a big facility. In a beautiful editorial we John Axe asked "whether the human spirit is lifted more by the knowledge of the mass of the top quark than the understanding of the shape of a snowflake." We must, at all costs, make the public understand that we are not searching to understand some exotic property of the neutron. Conferences like this one are therefore important steps in this direction.

3) We need to collaborate better across international borders. Here, again, the ILL has been an outstanding example, but when it came to the financial crunch for the SERC (the British funding agency) in 1991 they decided — against the almost unanimous recommendations of the British neutron scattering community — that the contributions to the ILL should be cut. Unfortunately, this has done great damage to the spirit of European collaboration built up over 20 years.

Without an increased effort in these three directions I predict that our 'supply' will reduce, notwithstanding the high level of demand. What chance of new sources of neutrons in the 21st century? Fusion reactors will provide a source, but neither steady state nor laser-driven machines will provide a qualitative leap in intensity over the projected spallation sources. For other 'new' sources we will have to await a revolution in nuclear physics; such revolutions are difficult as the episode of 'cold fusion' demonstrated.

I hope we succeed in this endeavor of keeping a reasonable level of supply into the 21st century — I am optimistic — but it also evident that the mode of working for scattering experiments is going to depend further on central sources, despite the objections of the Peter Egelstaff's! These sources (particularly any reactors that are built) are just too expensive for there to be any choice. In this respect I'm encouraged by the developments of Collaborative Research Groups at ILL (Participating Research Teams at NSLS) in which individual groups have a strong investment in the instrumentation. This allows for the training of younger people and for students to actively participate, rather than just perform an experiment at some 'user machine' (there is a place for them as well, of course). In this way we can re-capture some of that blend of small and big teams that is so successful for our future. For example, rather than the 50 instruments now at the ILL, why not have 100 beams? It's a matter that should be carefully considered by the planners of the ANS, ESS, and other future sources.

References


BORON-NEUTRON CAPTURE THERAPY FOR INCURABLE CANCER
AND INOPERABLE BRAIN TUMORS

Hiroshi HATANAKA
Department of Neurosurgery
Teikyo University
Kaga, Itabashi-ku, Tokyo 173, Japan

ABSTRACT

Recent advances in cancer diagnosis and treatment have not yet improved the survival rate of patients with cancers of the brain, liver, etc. In these organs, an extirpation of the organ, which can be done for stomach, breast, cervix, lung, etc., is not allowed, and this fact is the cause of poor therapeutic results.

Boron-neutron capture therapy (BNCT) utilizes the nuclear reaction which will take place between the boron-10 (loaded in the cancer cells artificially) and the thermal neutrons (delivered by reactors). The secondary radiations, helium and lithium, hit the cancer cell itself and cause the death of the cancer cell while sparing the surrounding normal cells.

BNCT in Japan has been applied to treating more than 130 brain tumor patients since 1968 by Hatanaka and collaborators. The longest surviving patient has lived more than 20 years. Nine patients have lived longer than 10 years with good quality of life.

BNCT is now being tried also by Oda of Kyoto University (9 cases) and by Nakagawa of Tokushima University (7 cases). It has been tried by Mishima (Kobe University) on 12 skin melanoma patients, proving satisfactory local control of the melanomas.

Mercaptoundecahydrodecaborate (BHS) and boronophenylalanine (BPA) have been tried for brain tumors and for melanoma.

For cancers of the liver and abdominal viscerae, antibody to the tumor specific antigen has been considered a good carrier of boron-10. Surgeons Takahashi, Fujii, Fujii, Yanagis, and Sekiguchi and immunologist Nariuchi of Tokyo University have been involved in the research and have obtained encouraging results in animals.

Bone cancers have been studied by veterinary surgeons Takeuchi, Kadosawa and others at Tokyo University by using boronated derivative of porphyrins (STPP) with satisfactory accumulation in the tumor tissue.

Hatanaka has been proving good effect of BNCT upon giant cerebral arteriovenous malformation (AVM) and skull base meningioma. These diseases, although pathologically benign, have posed difficult problems in neurosurgery. It will be exciting good news to the patients.

In conclusion, BNCT appears to be a good means to treat difficult lesions in the brain and other organs which defy sophisticated modern therapeutic means.
INTRODUCTION

Recent advances in cancer diagnosis and treatment have not yet improved the survival rate of patients with cancers of the brain, liver, etc. In these organs, an extirpation of the organ, which can be done for stomach, breast, cervix, lung, etc. is not allowed, and this fact is the cause of poor therapeu-
tic results.

Boron-neutron capture therapy (BNCT) utilizes the nuclear reaction which will take place between the boron-10 (loaded in the cancer cells artificially) and the thermal neutrons (delivered by reactors). The secondary radiations, helium and lithium hit the cancer cell itself and cause the death of the can-
cer cell while sparing the surrounding normal cells.

BNCT in Japan has been applied to treating almost 140 brain tumor patients since 1968 by Hatanaka and collaborators. The longest surviving patient has lived 20 years and 9 months. Nine patients have lived 10-21 years with good quality of life.

Since the discontinuation of clinical trials at Brookhaven and Boston in 1961, the concept of neutron capture therapy (NCT) had been practically for-
gotten until 1968, when the author resumed the treatment. Five years later in 1973, Professor Gordon L. Brownell of Massachusetts Institute of Technology, advocated for reassessment of neutron capture therapy in the treatment of cere-
bral gliomas at the 7th National Cancer Conference, after seeing the author's preliminary work. He was a collaborator of Professor William H. Sweet, then the Chief Neurosurgeon at Harvard, who had conducted the early American clin-
cical trials. In the preceding year, 1972, a 50-year-old patient with a glo-
blastoma was treated by BNCT by the author. He was the 10th case in the series, and ever since he has been alive and well for the past 25 years and 9 months. Although the term "cure" is a taboo word among cancer specialists, it would be safe to call him the first case that was 'cured' by neutron capture therapy.

The concept of NCT has become increasingly important because indication to this type of therapy is by now considered to include not only malignant brain tumors but also benign but inexcisable brain tumors, and other incurable cancers in other parts of the body.

1) Brain tumors

One-hundred and thirty-nine patients with intracranial tumors (139) and nerve-related extracranial tumor (one) were treated by boron-neutron capture therapy before last Friday (March 5, 1993) by the author and collaborators. Eighteen lived or have lived longer than 5 years out of 87 patients operated on before May 1987. Nine of these 18 lived or have lived longer than 10 years out of 53 patients operated on before May 1982.

Among more-than-10-year survivors, only two died at 17 and 12 years. All the others are still alive. The two died of delayed radiation damage because BNCT was applied to glioblastomas recurrent after their conventional radio-
therapy. They lacked evidence of tumors when they died.

Out of these 9 more-than-10-year survivors, three had been previously treated by conventional external radiotherapy and they developed radiation damage which brought all three patients ultimately to an incapacitated condition. Two of the three died. All the other six who were free from previous radiation history are active in their jobs and have no evidence of tumors: a farmer with glioblastoma, after 20 years, now at age 70; a school teacher with chondro-
sarcoma, after 15 years, now 45 years old; a 5th grader with astrocytoma, after 11 years, now a 22-year-old draftswoman; a woman with glioblastoma, af-
ter 15 years, now at age 75 still working as a lab assistant; a housewife with
transverse sinus meningioma, after 14 years, now 61 years old; and a hotel employee with parasagittal meningioma, after 14 years, now retired at the age of 72.

Glioblastoma patients can expect a 50% 5-year survival if the tumors are at the surface of the brain, and if treated within 2 weeks after discovery. This excludes radiotherapy or chemotherapy, but not a satisfactory debulking prior to BNCT. The procedure has to be performed avoiding iatrogenic tumor cell seedings. Brain stem gliomas, which do not allow even a debulking surgery, have been treated with some success.

Cerebral metastases from cancers can be easily controlled by a single radiation with BNCT.

Many patients with benign intracranial tumors (meningiomas, craniopharyngiomas, neurinomas, and many others) are eventually incapacitated and killed in some years. Hence they are called "clinically malignant".

Deep-seated inexcisable meningiomas of the cavernous sinus and clivus were treated by BNCT. Shrinkage of the tumors is recognized. One patient bedridden for 6 years stood up to walk.

BNCT on craniopharyngioma, which statistically kill most infant patients before adulthood unless they meet exceptionally skillful surgeons, and on bilateral acoustic neurinomas, which will make the patient totally deaf by ordinary surgery, has been contemplated.

2) Cerebral vascular malformation

Giant AVMs, which have defied surgical excision by master surgeons or radical obliteration with other types of radiosurgery (stereotactic gamma-unit and proton beam), seem to be effectively and safely treated by BNCT. Cerebral vascular malformations (CVM) which cause hemorrhage, seizure and other neurological problems, are found at autopsy in 0.3–0.1% of the population. Among them most frequent arteriovenous malformations (AVM) are corrected by total excision or total obliteration of the nidus, but only limited number of AVMs have been treated by skilled neurosurgeons. So far a total obliteration without destroying the surrounding brain matter has been achieved by other types of radiosurgery like stereotactic proton beam or gamma-knife, only if the lesion is small enough. A giant AVM has always defied treatments, and is a lifelong devastating disease.

Three AVMs were so far treated with a small dose of boron-10 neutron capture therapy. The plan has been to repeat such small dose irradiations 2–3 times with 0.5–one year apart. In Case 1, by the first round of BNCT irradiation, the AVM became significantly less contrast-enhanced on CT by the 5th day. Another CT obtained later showed even more improvement. The patient's complaint, intermittent severe headache, was gone and the patient returned to work after two months. Total obliteration of the AVM may be expected by one more round of BNCT.

The brain will not take up boron-10 isotope and hence will be relatively free from BNCT radiations. The vascular endothelium will be exposed to radiations arising from the boron-10 contained in the circulating blood after intravenous injection, which captures the relatively harmless slow neutrons delivered to the patient's head in a medical reactor. Although the normal blood vessels will be radiated with helium and lithium, as Kitao and Nydin separately calculated, the dose absorbed by the normal cerebral vessels will be only one-third of the total radiation that occurs in the normal blood vessels for geometrical reason. In contrast, most radiations will be absorbed by the vascular walls of AVM, because its nidus is a conglomerate of vessels and will absorb most of the heavy particles. Thus AVMs will be exposed to almost three times as much radiation as the normal cerebral blood vessels. Besides, an AVM vessel may be structurally premature and may take up some boron-10.
3) Thermal neutrons and deep tumors

If these mass lesions are not near the cortical surface, epithermal neutron beam may come to everybody's mind. But epithermal beam is not so easily available as thermal beams. Heavy water to be administered orally and intravenously or intrathecally will assist deeper penetration of thermal neutrons. Multiportal thermal neutron delivery also increases the flux in the middle of the cranial cavity as we have demonstrated by direct measurement of neutron flux with gold wires implanted under the brain. Use of epithermal neutrons was emphasized by the author much earlier, but its clinical application requires thorough studies on animals. A large half-value layer of 4.0 cm can be achieved even with thermal neutrons in contrast to 2.0 cm of ordinary thermal beam half-value depth.

Different from physicists' concept, selective and effective boron-neutron capture therapy is possible to treat any deep-seated brain tumors if thermal neutron penetration into tissue is helped by the combination of large aperture beam, partial replacement of brain water content with heavy water, and multiport radiation. A patient's case is presented.

This case was an 11-year-old boy with recurrent primitive neuroectodermal tumor (PNET) seeded in the lateral and the third ventricles, 3 years after a full course radiotherapy for the whole brain and the spine. After BNCT the patient recovered from semi-comatose condition and survived 1.5 years. Although he died of radiation damage due to overlapping radiotherapies, this case proved efficacy of BNCT on recurrent PNET.

FUTURE PROSPECT

BNCT is now being tried also by Oda of Kyoto University (9 cases) and by Nakagawa of Tokushima University (7 cases). It has been tried by Mishima (Kobe University) on 12 skin melanoma patients, proving satisfactory local control of the melanomas.

Mercaptoundecahydrododecaborate (BSH) and boronophenylalanine (BPA) have been tried for brain tumors and for melanoma, respectively. Several new boron compounds are also being developed.

For cancers of the liver and abdominal viscerae, antibody to the tumor specific antigen has been considered a good carrier of boron-10. Surgeons Takahashi, Fujii, Fujii, Yanagie, and Sekiguichi and immunologist Nariuchi of Tokyo University have been involved in the research and have obtained encouraging result in animals.

Bone cancers have been studied by veterinary surgeons Takeuchi, Kadosawa and others at Tokyo University by using boronated derivative of porphyrins (BTPP) with satisfactory accumulation in the tumor tissue.

Hatanaka has been proving good effect of BNCT upon giant cerebral arteriovenous malformation (AVM) and skull base meningioma. These diseases, although pathologically benign, have posed difficult problems in neurosurgery. It will be exciting good news to the patients.

In conclusion, BNCT appears to be a good means to treat difficult tumors in the brain and other organs which defy sophisticated modern therapeutic means.

REFERENCES

Phase Transitions and Neutron Scattering

G. Shirane
Brookhaven National Laboratory,
Upton, N. Y. 11973, U. S. A.

ABSTRACT

A review is given of recent advances in neutron scattering studies of solid state physics. I have selected the study of a structural phase transition as the best example to demonstrate the power of neutron scattering techniques. Since energy analysis is relatively easy, the dynamical aspects of a transition can be elucidated by the neutron probe. I shall discuss in some detail current experiments on the 100K transition in SrTiO₃, the crystal which has been the paradigm of neutron studies of phase transitions for many years. This new experiment attempts to clarify the relation between the neutron central peak, observed in energy scans, and the two length scales observed in recent x-ray diffraction studies where only scans in momentum space are possible.

INTRODUCTION

Over the years the neutron scattering techniques, in particular, triple axis spectrometers have played a major role in dynamical studies of structural phase transitions. The 100 K transition in SrTiO₃ is one of the most extensively studied. This was the first example of the zone boundary soft mode condensations¹ and was studied in 1969. Following this, the central peak was discovered by Riste et al² in 1971 and Shapiro et al³ subsequently characterized it in great detail. Recently a series of x-ray investigations⁴,⁵ reported the new phenomena of two length scales in SrTiO₃: (1) the "narrow" q peak only observable near Tc, and (2) temperature dependent thermal diffuse peaks originating from the soft modes. Similar two length scales were also reported⁶,⁷ for KMnF₃ and RbCaF₃. These observations prompted the current neutron scattering experiment⁸ in order to clarify the relation between the x-ray and neutron observations.

Fig. 1 demonstrates an example of energy scans of SrTiO₃, which consists of the soft mode peak at ΔE = ωₙ and the sharp central peak at ΔE = 0. The renormalized soft-mode frequency ω₀ is related to ωₙ by a coupling constant δ²

\[ \omega_0^2 = \omega_n^2 - \delta^2 \]  

(1)
under certain assumptions, the integrated intensities of these three peak structures are given by

$$
\int S(q, \omega) d\omega = \int S(q, \omega)_{\text{cent}} d\omega + \int S(q, \omega)_{\text{phonon}} d\omega
$$

$$
\frac{1}{\omega_0^2} = \frac{\delta^2}{\omega_0^2 \omega_\infty^2} + \frac{1}{\omega_\infty^2}
$$

(2)

It is the renormalized frequency $\omega_0$ which goes to zero at $T_c$ causing a divergence in the central peak and total integrated intensity (Fig. 1).

(A)

(B)

Figure 1

Fig. 1 (A) temperature dependence of $\omega_\omega^2$, $\omega_\omega^2$ and $\delta^2$ near the 100K transition in SrTiO$_3$ (B) Neutron profiles of side-band $\omega_\infty$ and central peak around $\omega = 0$. After Shapiro et al. 3)

Recent high resolution x-ray studies revealed a narrow and broad peak centered at the zone boundary position as shown in Fig. 2 Andrews$^4$ reported
Fig. 2 (A) two length scales observed by Andrews\textsuperscript{4} for SrTiO\textsubscript{3}. (B) Anisotropy of short length scale and isotropy of long length scale observed by Ryan et al\textsuperscript{7} for RbCaF\textsubscript{3}.

the first observation of two length scales in SrTiO\textsubscript{3} (Fig. 2a) and more accurate line width measurements were later presented by McMorrow et al\textsuperscript{5}). Fig 2b illustrates similar two inverse correlation lengths\textsuperscript{7} \( \kappa_{L1} \) and \( \kappa_{L2} \) for RbCaF\textsubscript{3}. The broad peaks (\( \kappa_{L1} \)) have Lorentzian profiles and are anisotropic, which reflects the anisotropic slopes of the phonon dispersion curves measured along the (100) and (011) directions about the R point. On the other hand, the narrow peaks (\( \kappa_{L2} \)) have a Lorentzian squared shape and are isotropic. The latter are observable only in a narrow temperature range near \( T_C \) (\( T-T_C \) / \( T_C \) \( \leq \) 0.05).

Now, what is the relation between the new narrow peak in \( q \) space observed in the x-ray experiment and the central peak in \( \omega \) space observed in the neutron studies? To clarify this point, it is necessary to characterize more precisely the \( q \) dependence of the central peak in terms of a neutron experiment. The soft phonon energy \( \omega^2_{\infty} \) follows a dispersion relation (\( q \) is measured relative to the zone boundary). This slope \( \alpha \) is known to be temperature independent\textsuperscript{3}.
\[ \omega_\infty^2(q) = \omega_o^2 + \alpha \, q^2 \]  

(3)

and depend upon direction; namely \( \alpha = 3200 \text{ meV}^2\text{A}^2 \) for (100) and \( \alpha = 1000 \text{ meV}^2\text{A}^2 \) for (011) for SrTiO\text{3}. Since integrated intensities of phonons are proportional to \( 1/\omega_\infty^2(q) \) the inverse correlation length \( \kappa_\infty \) is given by.

\[ \kappa_\infty(T) = \sqrt{\frac{\omega_\infty^2(T)}{\alpha}} \]  

(4)

The total integrated intensity is proportional to \( \omega_o^{-2}(q) \) (Eq. 2) and if we assume \( \delta^2 \) is \( q \) independent, \( \kappa_0 \) is given as:

\[ \kappa_0(T) = \sqrt{\frac{\omega_o^2(T)}{\alpha}} \]  

(5)

The quantities \( \kappa_\infty \) and \( \kappa_0 \) are calculated from the temperature dependence of \( \omega_\infty \) and \( \omega_o \) measured in ref. 3 and are plotted in Fig. 3 for the [011] direction for SrTiO\text{3}. Also shown are the inverse correlation lengths \( \kappa_{L1} \) and \( \kappa_{L2} \) determined by x-ray diffraction\textsuperscript{4,5}. The observed values of \( \kappa_{L1} \) lie between \( \kappa_\infty \) and \( \kappa_0 \), but closer to the latter. As \( T \to T_c \), both \( \kappa_\infty \) and \( \kappa_{L2} \) approaches zero; however \( \kappa_0 \) remains an order of magnitude larger than \( \kappa_{L2} \). Therefore the small value of \( \kappa_{L2} \) can not be explained by the central peak unless \( \delta^2 \) is strongly \( q \) dependent and decreases rapidly with increasing \( q \). This point can easily be checked by a neutron scattering experiment as described below.

As seen in Fig. 1, the central peak of SrTiO\text{3} can be easily separated out, in energy, from the phonon part, except for a very narrow temperature and \( q \) range near \( T_c \). Even in these areas, the intensity of the central peak dominates the spectrum and the high resolution neutron study probes essentially only the central peak (Fig. 4) If \( \delta \) is \( q \) dependent, the intensities of the central peak alone are given by (See Eq. 1 and 2).

\[ I_{\text{cent}} \approx \frac{1}{\kappa_0^2 + q^2} - \frac{1}{\kappa_\infty^2 + q^2} = \frac{\delta^2}{(\kappa_0^2 + q^2)(\kappa_\infty^2 + q^2)} \]  

(6)

This equation gives a Lorentzian like profile near \( T_c \) where \( \omega_\infty^2 >> \kappa_0^2 \) and its half width \( \kappa_c \) approaches \( \kappa_0 \) as \( T \to T_c \). At high temperature limits, it changes into a Lorentzian squared profile with \( \kappa_c \) approaching 0.64 \( \kappa_\infty \). If the basic
Fig. 3  The inverse correlation length $\kappa$'s derived for SrTiO$_3$. Open circles are current high resolution neutron data$^8$.

Fig. 4  Anisotropy of phonon dispersions observed for SrTiO$_3$. The lower figures illustrate similar anisotropy reflected in the central peaks at $\Delta E = 0$. These are results of the current joint experiment$^8$ with Cowley, Matsuda and Shapiro.

assumption of $q$ independent $\delta^2$ is correct, the observed profile of the central peak should reflect the anisotropy of $\kappa_{\infty}$ is in the $q$ space.

This key point is clearly demonstrated in Fig. 4, the data obtain at 115K. Moreover the observed line widths $\kappa_{\infty}(T)$ are in reasonably good agreement with the prediction of Eq. 6. The data taken near $T_c$ with the better resolutions revealed the same characteristics. The highest resolution obtained so far employed 4.4E$_{iv}$, 10' collimation throughout with a PG(002) monochromator and analyzer. The resolutions (FWHM) are 0.003-0.004 Å$^{-1}$, depending upon the direction of the scan. These values are only a factor of two or three larger than the x-ray resolution used in Fig. 2. We can now conclude that the central peak is an integral part of soft phonon cross sections over a wide range of temperature (up to 180 K) and $q$ (up to 0.1 Å$^{-1}$) and corresponds most closely with $\kappa_{1,1}$
measured with x-rays. It does not correspond to the narrow q peak \( q_{L2} \) in the x-ray profiles.

Can we conclude that the narrow component is missing in the neutron central peak profile? If so, the narrow peak must be highly localized in the near surface region or the "skin" of the crystal (a few microns) and can be detected only by x-rays. The answer is probably yes. But in order to be positive, it would be highly desirable to carry out neutron measurements with q resolution nearly identical to those of x-ray. This is actually possible for the current study, since the SrTiO\(_3\) crystal has a nearly perfect mosaic width of 7 seconds of arc\(^9\). Combined with a perfect Ge(220) analyzer, one can reach the resolution of 0.001 Å\(^{-1}\). This experiment, which is expected to be low counting, is now being planned.

What is the current physical picture of two length scales? The most attractive one is to assume two types of excitations\(^7\); one is the ordinary soft phonon within the framework of cubic lattice vibration. Impurities may create the central peak to modify the spectral weight. Another excitation of long length scale is a very different type of excitation into a tetragonal "embryo", near \( T_C \). This has a finite size, is isotropic; and with the size growing as \( T \) approaches \( T_C \). Most likely these "embryos" are highly populated near the surface so that it is more sensitive to x-rays.

The 100 K transition in SrTiO\(_3\) is second order and the tetragonal distortion below \( T_C \) is extremely small. KMnF\(_3\) and RbCaF\(_3\) both show first order transitions and the lattice distortion at \( T_C \) are 1.0009 and 1.0002 respectively\(^6,7\), within the detectable range of high resolution x-ray technique. There has been some experimental evidence presented \(^6,7\) that the narrow component just above \( T_C \) does not appear at the cubic R points but at the q point corresponding to the low temperature superlattice Bragg position. The lattice distortion is sufficiently large for KMnF\(_3\) and can be detected by high resolution neutron measurements\(^10\). In this case, the narrow peak should appear at a position slightly shifted from the central peak maximum; which would considerably enhance the detectability \(^10\).

Very recently, similar two peak structures are observed for magnetic critical scattering of Ho by Thurston et al\(^11\). In this case, neutrons see both broad and sharp components and x-ray see only the narrow one. Further study of other structural and magnetic phase transitions would reveal how common these two length scales are near \( T_C \).

ACKNOWLEDGEMENT

The current neutron scattering studies of SrTiO\(_3\) presented in this review are being carried out jointly with R. Cowley, M. Matsuda, and S. Shapiro and details will be reported soon. I would like to thank my colleagues, as well as S. R. Andrews, for many stimulating discussions. Work at Brookhaven was supported by the Division of Materials Science, U.S. Department of Energy under contract no. DE-AC02-76CH00016.
REFERENCES

9) J. R. Schneider et al., Phase Transitions 8, 17 (1986).
RECENT DEVELOPMENT IN MAGNETIC NEUTRON SCATTERING STUDIES

Yasuo ENDOH

Department of Physics, Tohoku University
Aramaki Aza Aoba, Aoba-ku, Sendai
980 Japan

ABSTRACT

Neutron scattering results contain many new concepts in modern magnetism. We review here the most recent neutron magnetic scattering studies from so-called "214" copper oxide lamellar materials, because a number of important developments in magnetism are condensed in this novel subject. We show that neutron scattering has played a crucial role in our understanding of modern magnetism.

INTRODUCTION

The most remarkable highly correlated electron systems are the lamellar copper oxide materials. Due to the strong electron correlation in d orbitals, $\text{La}_2\text{CuO}_4$, for instance, becomes an antiferromagnetic insulator of the charge transfer and it undergoes a metallic phase transition upon charge doping. Since the doped metals of these lamellar copper oxides exhibit the high temperature superconducting state, their fundamental properties have been extensively studied in various ways. Physics of the high temperature superconductor are so unusual that many data obtained from different experiments of transport, thermodynamic and magnetic properties should be interpreted consistently with a unified model. As far as we know, there exists no satisfactory theory to solve this subject. Among many experiments, neutron scattering plays an essential role providing unique data showing both static and dynamic spin fluctuations in microscopic scale, since the inherent relation between spins and electronic charges must be crucial for exploring the microscopic mechanism of the appearance of the high temperature superconductivity.

We have elucidated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystals systematically from $x=0$ undoped insulating antiferromagnetic state to $x=0.15$ doped superconducting state with $T_c=36\text{K}$, besides several reference compounds which
belong to the same family of so called "214" lamellar metallic oxides. The magnetism in the present system varies dramatically as the function of the doping concentration x. Therefore magnetism in "214" materials is extremely rich in physics. The aim of the present paper is to show several challenging data which contain the most recent development of neutron magnetic scattering studies. Therefore we will not specifically discuss the high temperature superconducting mechanism, but we will emphasize that only neutron scattering can probe such significant changes in spin fluctuations with very narrow range of x. Furthermore we raise many important issues in modern magnetism by taking such key words underlined in the following text that have been established in recent years.

**SPIN CORRELATIONS OF 2D HEISENBERG ANTIFERROMAGNET**

La$_2$CuO$_4$ can be metallic unlike many ceramic materials according to the band calculation$^4$. However this material, in fact, is an antiferromagnetic insulator due to the strong electron correlation effect in the copper d bands. Therefore the Fermi energy meets exactly in the energy gap splitted off by the large intra-atomic exchange interaction. Nearest neighbor Cu$^{2+}$ spins are thus coupled antiferromagnetically with each other by the 180 $^\circ$ superexchange interaction of Cu$^{2+}$-O-Cu$^{2+}$. The antiferromagnetism in La$_2$CuO$_4$ is not so simple as expected primarily due to an orthorhombic distortion (B$_{mnb}$) by the small rotation of the octahedron network of oxygen atoms surrounding Cu$^{2+}$ ions at the center. Cu$^{2+}$ spins are canted out of CuO$_2$ planes towards perpendicular direction to the plane by the antisymmetric exchange interaction, so called Dzyaloshinski-Moriya interaction.$^5$ When the magnetic field is applied along the perpendicular direction to the plane, a weak ferromagnetic moment is induced along the field direction. Another complication comes from the fact that the Neel temperature (T$_N$) at which the antiferromagnetic long range order (LRO) is established, decreases substantially with the existence of a small amount of excess oxygen.$^6$

Excess oxygen in La$_2$CuO$_{4.8}$ is considered to be immiscible and the chemical phase separation might occur.$^7$ Judging from the fact that T$_N$ is continuous as the function of 8, no such an evidence indicating the phase separation induced by excess oxygen inclusion has been obtained at least 8 is less than 0.03. Upon oxygenation of La$_2$CuO$_{4.8}$ the antiferromagnetic order parameter curve ultimately shows a reentrant behavior at low temperatures. Simultaneously enhanced central component of the magnetic diffuse scattering appears around the antiferromagnetic Bragg peak.$^8$ This spin glass behavior is reasonably explained by the frustration model.$^9$ Spins in the extra holes localized in oxygen orbitals
in CuO$_2$ plane couple antiferromagnetically with nearest neighbor Cu$^{2+}$ spins. Eventually the occurrence of the spin glass phase is seen in light doped La$_{2-x}$Sr$_x$CuO$_{4-y}$ system.

In this respect, La$_2$NiO$_{4+y}$ shows the immiscibility gap effect in magnetic properties$^{10}$. The fact that the stable La$_2$NiO$_4$ phase realizes only in the limited oxygen concentration very near at the stoichiometry range is a remarkable contrast to the case of La$_2$CuO$_{4+y}$ described above. There has been observed at least two immiscibility gaps as the function of excess oxygen concentration in the small range of $\delta$ ( $\delta < 0.07$).

Though the 3D antiferromagnetic LRO realizes by the weak magnetic interaction connecting CuO$_2$ lamellas, the intrinsic magnetism is dominated by the Heisenberg antiferromagnetic exchange interaction acting in the CuO$_2$ plane. Spin dynamics at low temperatures well below $T_N$ are reasonably described by the simple spin waves propagating in the plane. Inelastic neutron scattering shows a very clear evidence that a sharp resonance appears at $\omega - \omega_q$, where the spin wave dispersion, $\omega_q$ is simply approximated by $|\sin q_2D$. In order to complete the spin wave dispersion curve, the conventional 3 axis spectroscopy is not enough but the time of flight (TOF) method using the pulsed spallation source has been combined. Since the TOF method scans in a wide momentum space in the scattering plane at once, the scattering geometry can be chosen in such a way that a scattering locus satisfies the resonance condition at several points on the spin wave dispersion curve. The combination of the data collected by two complementary method determines the exact spin wave dispersion relations of both La$_2$CuO$_4^{11}$ and La$_2$NiO$_4^{12}$ and hence determines microscopic parameters of the magnetic exchange interaction and anisotropy which can be used to further analysis of thermal properties of spin fluctuations at finite temperatures.

At elevated temperatures, spin dynamics deviates from the simple spin wave modes toward thermal fluctuations restricted by the strong 2D antiferromagnetic spin correlations. Neutron magnetic scattering is coherent only in the plane. Correspondingly, when the scattering plane is taken in the reciprocal plane spanned by the $a^*$ and $c^*$ axes, magnetic scattering appears along the Bragg rods parallel to the $c^*$ axis, where the rods cross at $(h, 0)$ or $(0, k)$ with odd $h, k$. Energy integrated intensities which correspond to the instantaneous spin-spin correlation function, $\langle S(Q) S(-Q) \rangle$ were successfully analyzed by the theoretical models treating the 2D quantum Heisenberg antiferromagnetic system$^{11}$. Such theories treating the quantum effect which governs thermal spin fluctuations include either the renormalized spin wave velocity or the scaling function as the adjustable parameters. These values are often given by the model calculations but the direct evaluation can be made by using experimentally determined parameters mentioned above.
Another peculiarity is the large suppression of the critical spin fluctuations near $T_N$. The divergence of the correlation length towards $T_N$ usually induces the critical slowing down of fluctuation energy associated with the cross-over from the high temperature to the low temperature property; for instance, in this case, it shows the high temperature 2D Heisenberg type to the low temperature 3D XY or Ising type. In La$_2$CuO$_4$, the cross-over is unclear probably due to the strong effect of quantum fluctuations on spin dynamics. On the other hand, the dimensional cross-over was observed in La$_2$NiO$_4$\textsuperscript{13}. It is compared with the cross-over of the spin symmetry from Heisenberg to Ising in K$_2$NiF$_4$ near $T_N$\textsuperscript{14}.

**METAL INSULATOR TRANSITION AND SPIN FLUCTUATIONS**

Upon substitution of either divalent or tetravalent cations such as Sr, Ce etc. to La, electronic charges of either holes or electrons are doped. Eventually the metallic transition occurs at a certain doped concentration $x$. Unlike the Mott transition from insulator to metal, the effective mass never enhances near the transition. The 3D antiferromagnetic LRO seems to disappear simultaneously at the transition. One surprising result in the doped metals is the linear resistance with respect to temperature. It is interpreted by the presence of the spin susceptibility term in the resistivity expression where the charge and spin term is decoupled \textsuperscript{15}.

When we look at neutron magnetic scattering data from the doped crystals of La$_{2-x}$Sr$_x$CuO$_4$ with light doping $x$, we can clearly detect the change in the nature of spin dynamics as expected\textsuperscript{16}. Temperature dependence of the spin correlation length is well interpreted by the heuristic relation of the sum of the inverse correlation length, $\xi_0^{-1}$, which is related to the average hole distance, and that of the thermal correlation length, $\xi(T)^{-1}$ in the undoped La$_2$CuO$_4$. Dynamical spin susceptibility $\chi''(Q\omega)$ which is derived from neutron scattering intensity $S(Q\omega)$, is scaled by tan$^{-1}(y)$, where $y$ is given by $\omega/T$, for the wide range of both energy and temperature. Since this scaling behavior is theoretically given by either a model of the weak itinerant antiferromagnetism\textsuperscript{15} or a two band model\textsuperscript{17} in which the hole and electron bands at the Fermi energy nested by an exchange interaction. Though these models are different in detail, the important fact is that the scaling behavior of tan$^{-1}(\omega/T)$ in $\chi''(Q\omega)$ definitely indicates the metallic character in antiferromagnetism for the light doped crystals. It is also consistent with the result of the optical conductivity in high frequency \textsuperscript{17}, which shows a drastic change in conductivity even in the small $x$, although the weak localization behavior remains at low energies and low temperatures.
Finally we present another interesting result that the electron doped cuprates such as (Nd,Pr)$_{2-x}$Ce$_x$CuO$_4$\cite{18} show somewhat different magnetic properties from La$_{2-x}$Sr$_x$CuO$_4$. One major difference is that the insulator to metal transition occurs at higher concentration of $x$, about 0.15. $T_N$ changes more gradually with increase of Ce concentration $x$. Furthermore temperature dependence of spin correlation length, $\xi(T)$ is given by the similar function for La$_2$CuO$_4$ with the reduced spin wave stiffness constant from that of Nd$_2$CuO$_4$. The magnetic behavior is consistently explained by a scenario that electrons are mainly doped in Cu d orbitals. Therefore doping effect on the antiferromagnetism is well explained by the dilution effect since a doped site of Cu carries no local spins, when at least electrons are not mobile. Spin dynamics in Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-8}$\cite{19} is qualitatively similar to the result of La$_2$CuO$_4$, though the quantitative comparison remains in future experimental studies. In this respect, the recent experiment shows that Nd$_{2-x}$Ce$_x$CuO$_4$ always contains some excess oxygens in as grown state. Thus the random effect on the electronic state gives the extra localization effect, and the random effect must be removed by the heat treatment in reduction atmosphere which requires for the appearance of the superconductivity. This result is also consistent with the result of spin dynamics in heavy doped crystal of Nd$_{1.85}$Ce$_{0.15}$CuO$_{4-8}$. Essentially localized 2D antiferromagnetic spin dynamics realizes in as grown state, but for the sample annealed in a reduction atmosphere, inelastic neutron scattering corresponding to the antiferro-magnetic spin correlations cannot be seen, which might be hidden in the dominant incoherent scattering from Nd spin excited among the f electron ground state splitted by the crystalline field.

**SUPERCONDUCTIVITY AND SPIN CORRELATION**

Upon further doping $x$ by substituting Sr to La, superconductivity appears around $x=0.06$. The appearance of the superconductivity accompanies the incommensurate spin density wave (SDW) state, which will be described in the following paragraph. According to the recent experiments, the incommensurability is nonlinear with respect to the doping concentration $x$\cite{20}. We then speculate that the realization of the incommensurate SDW is established at $x=0.05$, which we consider to be associated with a complete mobile state. Nevertheless this conjecture must be confirmed in future experiments.

Extensive inelastic neutron scattering experiments have been performed mainly from $x=0.15$ crystal ( $T_c = 33K$ ) called KOSHU\cite{21}. The most remarkable feature in this KOSHU crystal is the magnetic structure of the 2D incommensurate SDW state where magnetic scattering appears at the reciprocal lattice vector incommensurate with the lattice.
periodicity presented by \((\pi, \pi + \delta)\) or \((\pi + \delta, \pi)\) in the tetragonal 2D reciprocal lattice\(^{22}\). \(\delta\) approximately saturates at 0.125 in the reciprocal lattice units in \(x=0.15\) crystal. It should be emphasized that magnetic scattering is not static but essentially inelastic.

\(S(Q\omega)\) shows quite unique features in both energy and temperature dependences. At lower energies as well as low temperatures, inelastic neutron scattering is sharp in momentum space, whereas it becomes broader in both higher energies and higher temperatures\(^{23}\). It is also very unusual that the scattering intensity is much larger in high energies than the low energy scattering. This fact is remarkable contrast against magnetic scattering from \(x=0.02\)\(^{24}\), which is understood within the framework of usual \textit{paramagnetic scattering} in metallic magnets. The spectrum is approximated by the Lorenzian in most of the case centered at the zero energy transfer. In other words, spectrum is weighted in lower energies. However the spectral weight of neutron magnetic scattering is reversed in superconducting crystals and almost no scattering in lower energies. Presumably the energy gap exists in spin excitations.

When we look at instantaneous spin correlations in heavy doped crystals where \(x\) is larger than 0.1, spin correlation length becomes short, which roughly accords with the average distance of nearest neighbor holes doped in the crystals. Judging from these facts, we can speculate that the higher energy part in inelastic neutron scattering may correspond to local spin fluctuations on Cu sites, and on the other hand, the low energy part varying with both temperature and energy might correspond to the spin fluctuations near the Fermi energy, which might be more related to the superconductivity.

Although the coupling between spin dynamics and superconductivity is not easily solved both theoretically and experimentally, the present neutron scattering results of many unusual features described above become significant issues in discussing the high temperature superconducting mechanism. For instance, a \textit{spin singlet} pairing between local and itinerant electron spins or a \textit{RVB} state is suggested\(^{25}\). The superconducting wave function might have an odd parity\(^{26}\) from the fact that neutron magnetic scattering persists in the superconducting phase below \(T_c\)\(^{27}\). These are few examples but most of the novel idea are still controversial which must be tested in future experiments. It should be emphasized here that neutron magnetic scattering experiments will continuously be contributed to the development in magnetism as an important probe.

Many more important novel subjects developed in recent years are not described, but without the significant role of neutron scattering, these subjects have not been proceeded. Namely these are the \textit{quantum effect} in the Heisenberg antiferromagnetic linear chain, the \textit{random field effect}, the anomalous phase transition due to the \textit{competing anisotropies}, the novel \textit{chiral order} in the triangular lattice, the \textit{spin slip}
in the helices of the rare earth metals, the heavy Fermion or Kondo lattice, the long range magnetic order by the interlayer coupling in the artificially designed materials of the magnetic multilayered films and etc.

The role of polarized neutrons to the experimental studies of magnetism will be more important in the future and therefore experimentalists must work hard to develop more sophisticated techniques to treat polarized neutrons. In this respect, we emphasize here that the depolarization measurements which studies the change of neutron polarization during the passage through the magnetic substance will open a new field. For instance, the magnetic structure in a mesoscopic scale can be studied readily\(^ {28}\); Magnetic flux motions in the mixed state of the superconductor, domain motions in ferromagnets, colloidal motions in ferrofluids are few examples.

ACKNOWLEDGMENTS

The most of the experimental results presented in the lecture have been mainly obtained at JRR3M in JAERI as well as HFBR in Brookhaven National Laboratory in US under the international collaborative project among Gen Shirane's group at BNL, Bob Birgeneau's group at MIT and Yasuo Endoh's group at Tohoku University. The author thanks many collaborators, but specifically, R.J.Birgeneau, M.A.Kastner, G.Shirane, T.R. Thurston, K.Yamada, M.Matsuda, K.Nakajima, M.Takeda, S.Itoh, S. Mitsuda, S.Hosoya, Y.Hidaka and N.Kojima. He is very happy that this collaboration has been extremely successful and joyful with frequent exchange of many ideas and intensive discussions.

The work has been supported by the Grant-in-Aid in the Priority Area in Scientific Research. The work also has been supported by the programs of Japan-US as well as Japan-UK neutron scattering collaborative projects. Both were sponsored by Japanese Ministry of Education, Science and Culture in Japanese side.

REFERENCES

11 S. Itoh et al., unpublished
13 K. Nakajima unpublished
20 Y. Endoh et al., J.JAP series 7, 174 (1992)
23 M. Matsuda et al., unpublished
26 T. Tanamoto, H. Kohn, H. Fukuyama, unpublished,
   N. Bulut, D.J. Scalapino, unpublished
EXPANDING THE FRONTIERS OF NEUTRON SCATTERING

Andrew TAYLOR

ISIS Facility
Rutherford Appleton Laboratory
Chilton, Oxfordshire, OX11 0QX  UK

ABSTRACT

Accelerator based pulsed neutron sources have in recent years significantly expanded the frontiers of neutron scattering as a microscopic probe of the condensed states of matter. This paper discusses why such sources have been developed, and what their advantages are over conventional steady state sources. Particular reference is made to the most advanced of the present generation of pulsed neutron sources, the UK pulsed spallation source ISIS. Scientific advantages are illustrated using recent examples of structural and dynamical studies from the science programme at ISIS. The development potential of pulsed sources, both in terms of new instrumentation and new sources, is also discussed, with particular reference to the proposed European Spallation Source.

INTRODUCTION

Neutron scattering underpins our microscopic understanding of the structure and dynamics of condensed matter in fields as diverse as Biology, Materials Science, Chemistry, the Earth Sciences and Physics. In many ways neutrons are a unique and ideal probe:

• Neutrons interact with atoms principally through the short range nuclear force, which varies irregularly from nucleus to nucleus. Light atoms may often be studied in the presence of heavy ones, and significant differences in the interaction generally exist between different isotopes of the same element. Undoubtedly the most widely exploited isotopic difference is that between hydrogen and deuterium. By the process of selective deuteration, neutron experiments are able to examine parts of complex molecules in many fundamental areas of chemistry, polymer science and biology. Soft condensed matter studies using neutrons have grown explosively over the last decade, and the problems being addressed now impinge significantly on the commercial world.

• The energy and momentum of neutrons may be matched simultaneously to energy and length scales appropriate for excitations in condensed matter. Neutron wavelengths of 1 - 10 Å are ideal for the study of interatomic correlations and the available neutron energies of 1 to 1000 meV allow the measurement of excitations over nine decades from neV to eV.
• The neutron has a magnetic moment which couples to spatial variations of the magnetisation of materials on the atomic scale. Neutrons are thus ideally suited for the study of magnetic structures (and hence microscopic magnetism) and short wavelength magnetic fluctuations. A recent example of this kind of measurement is the mapping out of the dynamical susceptibility of high $T_c$ superconductors, thus directly addressing the question of electron-electron correlations in this important class of new materials.

• The neutron is a weak probe, and does not significantly perturb the system. The resultant data may be directly compared with theory. In many cases absolute cross-sections may be obtained. This must be contrasted with the difficulties in interpreting information from strongly interacting probes such as photons or electrons.

• The low absorption of neutrons and the lack of charge allows neutrons to probe the bulk of materials. This feature, which has made possible the construction of sophisticated sample environment equipment, is now being exploited in the study of residual stress in engineering components and composite materials.

In one aspect however, neutrons are far from being an ideal probe: the brightness of present day neutron sources are severely limited by the difficulty in removing the heat associated with neutron production. The world’s brightest steady state source of neutrons for condensed matter research, the Institute Laue Langevin in Grenoble, is required to dissipate 57 MW of heat to produce a flux of $1.5 \times 10^{15} \text{ n/cm}^2\cdot\text{s}$. Pulsed spallation sources circumvent the problem of heat dissipation in two ways. Firstly the spallation process is much more efficient (in heat terms) than fission: the cost of producing a neutron by spallation is some 30 MeV, compared with 190 MeV for the fission process. Secondly, accelerator based sources can be switched on and off in an easy and natural way, with a pulse duration of order a $\mu$s repeated on a timescale of, for example, 20,000 $\mu$s (corresponding to a repetition frequency of 50 Hz). Hence the heat produced during the $\sim \mu$s pulse may be dissipated during the 20000 $\mu$s interpulse interval.

Although the time averaged flux of such a source is modest, a peak flux much brighter than is possible with steady state sources can be realised with present day accelerator technologies.

To realise fully the potential of such sources requires the use of time-of-flight techniques. In general these sources are undermoderated so as not to degrade the pulse length. This has the consequence of producing a rich epithermal spectrum in addition to the familiar maxwellian distribution characterised by the temperature of the moderating material. These two aspects of pulsed spallation sources, the rich epithermal spectrum and the use of time-of-flight techniques naturally lead to a number of advantages which have been exploited to expand the frontiers of neutron scattering.

† Fission sources can also be pulsed, but with a much broader pulse duration (typically 250 $\mu$s for the Dubna IBR-2 source).
ADVANTAGES OF A PULSED SPALLATION SOURCE

• High brightness and excellent signal-to-noise: The source is essentially 'off' when data are collected, and so background from penetrating fast neutrons may easily be discriminated against by time-of-flight. This favours, among other things, the study of small samples and low cross-section processes.

• High intrinsic resolution in Q and \( \omega \): The high resolution is a natural consequence of the sharp 1 \( \mu \)s proton pulse. Moderation broadens somewhat the resultant neutron pulse, but since this pulse broadening and the flight time are both proportional to wavelength, the resulting ratio -- the resolution -- is essentially independent of wavelength and improves linearly with the length of the flight path. If \( t \) is the flight time in \( \mu \)s, \( \Delta t \) the pulse width, \( L \) the flight path (in m) and \( \lambda \) the wavelength in \( \text{Å} \) then

\[
t = 252 \lambda L \quad \text{and} \quad \Delta t \sim 7 \lambda \quad (\mu \text{s-m-Å})
\]

hence

\[
\Delta t/t = 1/36L = \text{very good} \quad (\text{eg 0.3% at 10m})
\]

In all fields, from astronomy to microscopy, improving resolution improves the scientific potential, revelling more and more subtle effects.

• Wide spectral range - from \( \mu \text{eV} \) to \( \text{eV} \): In addition to the \( \mu \text{eV} \) and \( \text{meV} \) neutrons familiar from steady state sources, the existence of a rich spectrum of epithermal neutrons with energies up to an \( \text{eV} \) and beyond, allow a whole new range of processes, in both space and time, to be studied.

• Wide dynamic range in data, both in terms of scalar (and vector) momentum transfer, energy transfer and signal-to-noise, allows the dynamics of processes to be measured, often simultaneously, over a wide range of time and length scale. Sensitivity to such a broad response allows the 'whole picture' to be seen rather than some narrow preconceived aspect. The corollary is that a vast volume of data is collected, emphasising the need to develop sophisticated methods of data visualisation.

• Fixed scattering geometry. In particular the use of a collimation and detection system at 90° to the incident beam greatly facilitates the use of complex and extreme sample environments such as chemical reaction vessels or pressure cells

• Pulsed nature itself. This naturally leads to studies of time dependent perturbations, kinetic experiments such as \textit{in situ} chemical reactions, and the exploitation of extreme conditions which cannot be achieved in the steady state.

• Simultaneous diffraction and inelastic scattering: This has been shown to be invaluable in many fields where a complex phase has been prepared in situ (eg liquid crystals, molecules adsorbed or intercalated) and the exact state must be monitored simultaneously with the measurement of the excitations.
UK PULSED SPALLATION SOURCE ISIS

The ISIS Facility is the most powerful of the present generation of pulsed neutron sources. It is driven by a high current 800 MeV proton synchrotron which delivers 0.4 μs pulses of protons onto a heavy metal target at a repetition frequency of 50 Hz. First operational in 1985, ISIS has now reached its design goal of 200 μA. The plated target of depleted uranium (25 n/p) or tantalum (12 n/p) is cooled by D₂O and surrounded by a D₂O-cooled beryllium reflector. Three small (10x10x5 cm³) hydrogenous moderators (ambient water, 100 K liquid methane and 25 K liquid hydrogen) are viewed by 18 neutron beams. The ISIS Facility presently has 15 neutron instruments. ISIS operates for some 4000 hours per year. Latest results can be found in the ISIS annual report ISIS 93.

ISIS INSTRUMENTS

Figure 1 Layout of the ISIS Experimental Hall

Illustrations from Diffraction Studies at ISIS:

The high resolution and high Q information available on the 100 m HRPD instrument at ISIS allows multi-parameter refinements using data from powder samples. Studies of benzene have shown that refinements of atomic positions and anisotropic temperature factors can be obtained of a quality normally associated with single crystal data. This has an important impact on fields as diverse as geology, and pharmacology where single crystals are often not available, and detailed structural information is required. In the case of drug molecules, this allows a correlation between shape and biological activity to be studied.
High brightness and good signal to noise give the ability to study small samples. One example is recent work on the system \((\text{Pb,Cu})\text{SrLaCuO}_5\) where only 20 mg of the 30 K superconducting phase was available. A 10 hour run on POLARIS gave data of sufficient quality to allow a full Rietveld refinement, leading to an analysis of the disorder of oxygen in the charge reservoir layer.

Wide dynamic range is important in studies of disorder in many systems. An example is proton disorder in ice which gives rise to diffuse scattering. White beam Laue techniques allow large volumes of reciprocal space to be simultaneously observed.

Fixed geometry white beam techniques have been exploited in the Paris-Edinburgh high pressure cell. Full Rietveld refinement on Ice\text{VII} at 10 GPa has recently been achieved.

New materials such as \(\text{C}_60\) are often initially only available in limited quantities. Nevertheless, subtle analysis is often essential to understand fully their intrinsic properties. The recent discovery of the orientational glass transition at \(~90\ \text{K}\) in \(\text{C}_60\) needed a combination of high resolution, high intensity and good signal to noise: HRPD was able to measure lattice parameters to a part in \(10^6\) on less that one gram of sample and perform a temperature scan in 2 K steps (at 15 minutes a point) from 300 K to 20 K.

Illustrations from Dynamical Studies at ISIS:

Excitations are generally weak and benefit significantly from the high brightness and good signal to noise available on pulsed sources. Combined with the high available flux of epithermal neutrons, this has allowed, for example, weak intermultiplet processes in rare earth and actinide f-electron systems to be observed for the first time. The highest energy magnetic excitation observed to date is the 1776 meV \(3\text{H}_6\) to \(3\text{F}_6\) transition in thulium metal. The inherently low cross-section for this process is further reduced by form factor considerations since the associated momentum transfer is \(18\ \text{Å}^{-1}\). Other high energy processes which become accessible include recoil scattering from quantum systems such as \(\text{^4He}\) liquid, where final state interactions result in an oscillation of the width of the recoil line as a function of momentum transfer.

The dynamics of \(\text{C}_60\) and its superconducting derivatives manifests itself in several ways. In the frequency domain, the energy scale of interest extends from \(~1\ \text{meV}\) for the quasi-elastic scattering which freezes into librational modes below the 260 K phase transition, to high frequency modes \(~200\ \text{meV}\) thought to be associated with the superconducting mechanism. In the momentum transfer domain, a complex intensity modulation (an interference between various spherical harmonics) reflects the geometrical re-orientation of the molecule. The UK-Japan collaboration spectrometer MARI allows an overview of both the frequency and momentum transfer behaviour to be simultaneously determined: one dimensional scans would be a poor substitute.

The study of excitations in single crystals has long been thought to be the province of steady state sources because of the tremendous versatility of the triple axis spectrometer. However,
substantial progress has been made in recent years with the time-of-flight spectrometers HET and MARI at ISIS. The rich epithermal spectrum has been exploited to study itinerant magnetism in the transition metals, where the magnon dispersion curve has been followed in cobalt and iron to the zone boundary at 300 meV 550 meV respectively. Spin waves in the two dimensional high T_c parent system La_2CuO_4 have been observed up to the zone boundary at 312 meV. These spectrometers have shown themselves to be very effective indeed in the study of low dimensional systems, where the geometry of the large, background free, low angle detector arrays can be fully exploited. Novel quantum ground states have been studied effectively in a variety of low-spin one dimensional systems at energies of a few tens of meV.

DEVELOPMENT OF PULSED SPALLATION SOURCES

Improve performance of present sources. The performance of the present generation of pulsed spallation sources can still be significantly improved. A useful metric is the product of the average current the source produces, the time it operates and the number of instruments it schedules. This metric for ISIS is ideally 20,000 (200 μA x 5000 hr x 20 instruments), more than a factor two greater than the 9000 actually achieved in 1992.

Improve present instrumentation and sample environment. Improved exploitation of the present instrumentation is still possible. An example is the detector solid angle which, for financial reasons, is often less than ideal. The area of sample environment is also one where substantial advances, for quite modest outlays, are possible.

Develop new instrumentation and sample environment. Experience in the past ten years has lead to new instrument concepts and ideas for advanced sample environments. An example is the MAPS project where a second generation pulsed neutron instrument, specifically designed for the observation of excitations in single crystals has been proposed. Substantial advances in extreme environments, eg high magnetic fields, have also been proposed.

Improve the utilisation of present day sources. Some characteristics of present days sources are compromises. On ISIS the 50 Hz choice of repetition frequency, is a compromise between instruments such as HET and MARI which would prefer 100 Hz, and HRPD and LOQ which prefer 10 Hz. The choice of decoupling energy and moderator geometry further adds to the compromise. Accelerator driven sources easily lend themselves to the use of multiple target stations, and for a relatively modest investment, a customised low frequency target station optimised for long wavelength and high resolution studies could be realised.

Upgrade source strength. Accelerator development has gone on apace in the past decade.. Although ISIS is the most powerful pulsed source available today, its 160KW beam specification is modest compared with the 400 MW being discussed eg for accelerator transmutation of waste or isotope production. By this scale modest systems in the 1-5 MW range which would greatly exceed present day sources seem quite modest. There are currently design studies in Japan the US and Europe for accelerator based sources with power levels of 1 MW and above.
EUROPEAN SPALLATION SOURCE

Following an initiative by KFA Jülich and Rutherford Appleton Laboratory in 1991, a series of pan-European meetings were held to explore the options for a next generation pulsed spallation source, the ESS. The following specification emerged:

- Power: 5 MW
- Pulse width: ~1us
- Frequency: 10 Hz and 50 Hz target stations.

Figure 2 The performance of the ESS is 30 x ISIS. The time-averaged flux is equivalent to ILL but pulsed, resulting in a qualitatively different source.

A proposal for a conceptual design study and costing exercise for a 5 MW ESS is currently underway in Europe. The expected scientific impact of the ESS is discussed in the proceedings of an Expert Meeting held under the auspices of the Commission of the European Communities in 1992 (available as RAL-92-040).
CONCLUSION

The frontiers of neutron scattering have been extended by the exploitation of high intensity pulsed spallation sources specifically designed for condensed matter research. Opportunities at such sources are qualitatively different from those at traditional steady state sources. The expectation for further extension of the sophistication of the instrumentation and strength of such sources in the near future is good in the United States, Europe and Japan.

Acknowledgements. It is a pleasure to thank friends and colleagues at IPNS, ISIS, KENS, LANSCE and on the SNQ, SINQ and ESS projects whose ideas have contributed to this paper.
ALLOYS STUDIED BY NEUTRON SCATTERING

Yukio MORII

Department of Physics, Japan Atomic Energy Research Institute
Tokai, Ibaraki 319-11 Japan

ABSTRACT

Neutron scattering study on the martensitic transformation and spinodal decomposition of alloys is described. Lattice vibration mode [110]TA1 in various noble metal bcc-based alloys was measured. An analysis of the (110) interplanar force constants revealed a relation between the force constants and the martensite phase at low temperatures. Time resolved experiments of spinodal decomposition of MnCu were carried out to investigate how the separated (decomposed) phase grows in time. In the late regime of the decomposition, the size of the precipitate increased with a power law of $t^{0.37}$ while the crystallite grew as $t^{0.236}$.

INTRODUCTION

It is very important to understand phase transitions of alloys in materials science. Extraordinary mechanical properties of alloys such as pseudo-elasticity, shape memory effect and high damping property are related to the martensitic transformation which is the first order phase transition with diffuse-less or displacive character. It is well known, for example, that some of the antennas in space are produced using the shape memory effect of TiNi. When a folded antenna, which is prepared in the martensitic phase, is warmed up to the parent phase, it opens and deforms to the shape just like it was in the parent phase as if the alloy remember the initial shape. Folding the antenna in the martensitic phase which produces big strains does not make a permanent deformation but the deformation by variant coalescence on stressing or the growing of one of the variants in the martensitic phase. Since no defects are introduced in the microscopic structure during the deformation, recovery of the original shape can be made a reverse transformation on heating.

The kinetic of the first order phase transition has also been a prime interest because of its technological importance in materials science. Phase separation of the alloys is observed when external variables change across the phase boundary. During heat treatment of multi-component system, an unexpected phase separation may produce harmful phases. Beside the practical
interests, it is understand that nonequilibrium phenomena, nucleation and growth, and pattern formation take place, if the external variables changes rapidly. These phenomena become of great interest in physical researches. Spinodal decomposition is a phase separation in unstable region which provides a typical example of the kinetics of the first order phase transition.

In this paper described are neutron scattering studies on the martensitic transformation and the spinodal decomposition of alloys to show how the neutron probe has been utilized in this field.

**MARTENSITIC PHASE TRANSFORMATION**

Martensitic transformations are observed not only in TiNi alloy but also in noble metal bcc-based alloys such as CuAlNi, CuZn, AuCuZn, AgCd, and AuCd which have moderate lattice instability in the parent phase. Although there is another group of alloys such as Indium, Al5 compounds and Manganese which have drastic lattice instability and the third group of alloys such as Iron and cobalt which demonstrate irreversible martensitic transformations, I will discuss only on the first group here.

Noble metal bcc-based alloys have anomalously low elastic constant $C'=(C_{11}-C_{12})/2$ compared to the other elastic constants which are measured by ultrasonic experiments. 1) Since elastic constant $C'$ is directly related to transverse acoustic phonon mode [110]TA1 of which wave-vector is in [110] direction and polarization vector $\mathbf{e}$ is in [110] direction, the slope of the dispersion curve, $\partial E/\partial q$, at the zone center is expected to be small therefore its phonon energy is expected to be small. This is one of the lattice instabilities which is related to the martensitic transformation in the first group of the alloy.

Since inelastic neutron scattering is enable us to measure phonon energy directly, the phonon dispersion curves of CuAlNi alloy was obtained at room temperature by Hoshino and others in 1975. 2) They clearly showed that [110]TA1 mode has anisotropically and anomalously low energy at all wave-vectors. Why the mode is so anomalous? Because this mode has the same atomic motion as the displacement in the martensitic transition of the alloy.

The martensitic phase transition is displacive, and the basal plane in the CuAlNi system is (110) plane. The [110] and [001] axes in the parent phase turn to be the [100] and [010] axes in the martensite phase. The martensite phase has stacking structure of the basal plane and various stacking types such as $\gamma_1$' or 2H, $\beta_1$' or 18R, $\alpha_1$' or 6R and $\beta_1''$ or 18R according to external conditions. It is very important to recall the basal planes shuffle toward [110] direction and the propagation of the shuffling is toward [110] which is the same as [110]TA1 phonon mode.

**FORCE CONSTANT ANALYSIS**

By means of neutron inelastic scattering, the author and his co-workers have extensively studied the [110]TA1 phonon mode of noble metal bcc-based alloys at JRR-2 of JAERI. 3,4) The [110]TA1 mode of the $\beta_1$-Cu69.2Al25.4Ni5.4 alloy has the temperature dependence of its energy at the temperatures well above the Ms (martensite starting) temperature, 256K, as shown in Fig. 1.
The figure clearly shows the "dip" in the dispersion curve around 2/3 of $q_{\text{max}}$. To understand the deformation of the dispersion curve, We have evaluated force constants between the (110) planes from the [110]$\tau_{11}$ phonon dispersion relation as shown below.

$$M\omega^2(q) = \sum \Phi_n (1 - \cos n\pi q/q_{\text{max}})$$  \hspace{1cm} (1)

where $M$ is the mass of atoms and $q_{\text{max}}$ is the wave vector corresponding to the zone boundary. Although the nearest neighbor force constant, $\Phi_1$, is dominant, the second and the third nearest neighbor force constant, $\Phi_2$ and $\Phi_3$, have a characteristic feature of the lattice instability in the martensitic transformation. We found that the second nearest neighbor and the third nearest neighbor force constant are both positive for the CuAlNi alloy and the CuAlZn alloys which have 2H type martensite. On the other hand, AuCuZn system which transforms to 9R type martensite has negative second nearest neighbor force constant as shown in table 1.

<table>
<thead>
<tr>
<th>#</th>
<th>Alloy Name</th>
<th>$\Phi_1$</th>
<th>$\Phi_2$</th>
<th>$\Phi_3$</th>
<th>$\Phi_4$</th>
<th>$\Phi_5$</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu$<em>{68.2}$Al$</em>{25.4}$Ni$_{5.4}$</td>
<td>293K</td>
<td>2.490</td>
<td>0.331</td>
<td>0.271</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cu$<em>{70}$Al$</em>{23}$Zn$_7$</td>
<td>293K</td>
<td>2.293</td>
<td>0.399</td>
<td>0.235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cu$<em>{68.4}$Al$</em>{21.1}$Zn$_{2.5}$</td>
<td>293K</td>
<td>2.052</td>
<td>0.308</td>
<td>0.167</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>E-T2</td>
<td>523K</td>
<td>0.555</td>
<td>0.470</td>
<td>-0.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Cu$<em>{70}$Al$</em>{25}$Zn$_{20}$</td>
<td>293K</td>
<td>2.013</td>
<td>-0.212</td>
<td>0.177</td>
<td>0.217</td>
<td>0.127</td>
</tr>
<tr>
<td>6</td>
<td>Au$<em>{68.2}$Cu$</em>{25.4}$Zn$_{5.4}$</td>
<td>293K</td>
<td>1.891</td>
<td>-0.298</td>
<td>0.407</td>
<td>0.094</td>
<td>0.123</td>
</tr>
<tr>
<td>7</td>
<td>Au$<em>{68.2}$Cu$</em>{25}$Zn$_{50}$</td>
<td>293K</td>
<td>0.515</td>
<td>-0.239</td>
<td>0.231</td>
<td>0.079</td>
<td>0.120</td>
</tr>
<tr>
<td>8</td>
<td>Au$<em>{68.2}$Cu$</em>{25}$Zn$_{47}$</td>
<td>293K</td>
<td>0.804</td>
<td>-0.361</td>
<td>0.306</td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CuCl$_2$</td>
<td>293K</td>
<td>0.183</td>
<td>0.259</td>
<td>0.129</td>
<td>0.088</td>
<td></td>
</tr>
</tbody>
</table>

Table 1  (110) interplanar force constants of various alloys
We also investigated the phonon dispersion curve of the Ag50Zn50 alloy which has stress induced 2H type martensite phase. We found again that AgZn has phonon anomaly in [110]TA1 as shown in Fig. 2. It is also found that the second and the third nearest neighbor force constant are positive at room temperature. When temperature is raised to ζ-phase, Φ2 decreases to negative as listed in the table 1, this is probably because diffusion mechanism is involved in the transition to ζ-phase. As a summary of the force constant analysis, the alloy which has 2H type martensite induced either by heat or stress have positive force constants, on the other hand, those alloys which have 9R type martensite have negative Φ2. Therefore we can predict which type of martensite will be produced by the force constant analysis.

![Phonon Dispersion Curve](image)

**Fig.2** Phonon dispersion relation of β1-Ag50Zn50. Open(Solid) circles represent measured transverse(longitudinal) acoustic phonon energies. Dotted lines are guides to the eye. The horizontal axis is the reduced wave vector, aq/2π, based on bcc structure. The folded Brillouin zone for the ordered structure of the alloy is shown by dashed lines.

**SPINODAL DECOMPOSITION**

Phase separation in general is observed not only alloy system such as FeAl, FeCr, AlZn, MnCu but also in simple fluid, binary fluid, glasses and crystalline ceramics and polymer blends and others. Phase separation in alloys and semiconductor is very important because decomposition of impurities usually causes deterioration of its quality. When a mono-phase is cooled and hit the two phases coexistence curve, two phases are produced. One of them has concentration C_a and the other has C_b. In the unstable region the spinodal decomposition takes
place. An example of the separation in FeAl alloy system after quenching from 630°C to 570°C was studied by Oki et al. They transmitted electron microscopy study clearly shows that the spinodal decomposition and subsequent coarsening of an unstable state of the system.

To study spinodal decomposition, we chose Mn67Cu33 system for a neutron scattering study because the sample is a disordered null matrix so that it has zero coherent neutron scattering or the minimum background scattering. Both Mn-rich and Cu-rich phases have virtually identical fcc lattice parameters so that it gives the minimum strain energy. After a rapid quenching from 800°C to 450°C in 30 seconds. We measured time dependent decomposition phenomena by the Small Angle Neutron Scattering machine (SANS) and the Wide Angle Neutron Diffractometer (WAND) at the HFIR of the ORNL.

From SANS experiments, we found that the kinetics can be described by the following three stages. 1. An initial stage where Cahn-Hilliard-Cook (CHC) theory works with a constant peak position, 0.098 Å⁻¹, of the structure function. 2. An intermediate stage. 3. A late stage where Furukawa's scaling law is obeyed with the fitting constant q in his universal scaling function equal to 4.8. It is also found that the measured peak position, Qmax(t), of the structure function, which is inversely proportional to the average domain size of the precipitates, is remarkably well fitted for the entire time region to equation 2 which is a modification from Huse's correction to the asymptotic power behavior of t in the late stage.¹⁰

\[ \frac{Q_{\text{max}}(t)}{Q_0} = (t/\tau)^{-n} \]

\[ n = 1/3 - A/(t/\tau)^{1/3} - A \ln(t/\tau) \]  

(2)

where \( Q_0, A, \) and \( \tau \) are the constants.

Figure 3 shows the experimental results for \( Q_{\text{max}}(t) \) and the fitted curve (eq.2) with the constants 0.0995 Å⁻¹, 0.293, and 100.2 seconds for \( Q, A, \) and \( \tau \) respectively. The three time stages of the evolution of the new phase are also shown in the figure.

![Graph showing the evolution of the new phase](image)

Fig. 3 The measured peak positions of the small angle scattering structure function, \( Q_{\text{max}} (\text{Å}^{-1}) \), are shown as a function of reduced time \((t=100.22\ \text{sec})\). The solid line is the result of fitting eq. 2 to the data.
KINETICS OF THE CRYSTALLITE IN THE PRECIPITATE

The Bragg peak gives information on the crystallites in the precipitate. The intensity of the Bragg peak is proportional to the volume of the crystallites, and the time dependence of the width of the peak is related to the particle size of the crystallites. The WAND is a powerful diffraction machine for the study of the kinetics of the phase separation since it covers 130 degrees in two theta angle simultaneously with moderately good angle resolution and has a time resolving data acquisition system. A wavelength of 1.537 Å was chosen. The Mn₆₇Cu₃₃ sample, which is the same one as used with the SANS, was placed in the rapid quench furnace and annealed at 800 °C or 30 minutes and then quenched to either 450 or 500 °C in 30 seconds. As discussed before, the disordered phase gave no coherent scattering at 800 °C. The Full Width at Half Maximum (FWHM) of the Bragg peaks were studied in situ from immediately after quenching for about 35 hours. The evolution of the Bragg peak indicated the growth of the new phase. The Bragg peak was broad when it appeared. Since the lattice constants of the two new phases are close to each other, only one peak was observed. The width of the peak decreased as the peak grew. Assuming that the mosaic spread of the small particles of which average size is less than one hundred angstroms is independent of the particle size, the time dependent part of the width is caused mainly by particle size broadening from the crystallites. Since the neutron scattering Bragg peak of the sample is well described by a Gaussian function, the time dependent particle size term of FWHM, B_p_s(t), is related to the observed width, B_{exp}(t), by the following equation 3.

\[ [B_{exp}(t)]^2 = [B_{instr}]^2 + [B_{p_s}(t)]^2 \]  

(3)

where \( B_{instr} \) is a time independent constant reflecting the instrumental width. \( B_{instr} \) involves all kind of extraneous source of broadening, therefore it was measured using a standard powder sample Al₂O₃ in which the particle size is large enough to eliminate all particle size broadening.

Figure 4 shows the square of \( B_{p_s}(t) \) for the (111) peak of the crystallite of the precipitate versus time on a logarithmic scale. Data between 10 and 300 minutes at 450 °C are

![Graph showing FWHM² vs. time for Mn₆₇Cu₃₃ samples at 450 °C and 500 °C](image)

Fig. 4 The time dependence of the square of the Full Width at Half Maximum (FWHM) of the (111) Bragg peak of the new phase which displays the particle size broadening. The solid fitting lines are based on a fit of the power law, \( n \), as a function of time to the FWHM.
well fitted to the power law $B_0 t^n$ where $B_0$ is an adjustable parameter. The fitted parameter $n$ is evaluated -0.236 for the 450C.

The particle size $L(t)$ is related to the FWHM, $B_{p,s}(t)$, by the Scherrer equation below,

$$B_{p,s}(t) = \kappa \lambda / L(t) \cos \theta$$  \hspace{1cm} (4)

where $\kappa$ is Scherrer constant for a cubic particle with edges of length $L(t)$, $\lambda$ the wavelength, and $\theta$ the Bragg angle. Solid circles in figure 5 show the calculated $L(t)$ on a logarithmic time scale. The particle size $L(t)$ is constant at 30 A within 10 minutes after quenching then increases with a power law of $t^{0.236}$ until about 365 minutes when the instrumental angle resolution limited the analysis of the width. The lattice size at 365 minutes is 68 A.

![Graph showing the growth of crystallite size over time](image)

**Fig. 5** The growth of the averaged particle size of the crystallites (solid circles) and the polycrystal precipitate (open circles) in the phase separation obtained with WAND and SANS respectively.

Open circles in the Fig. 5 are the average cluster diameter obtained by SANS experiments to compare the particle size of the crystallites in the late time regime ($t > 72$ min). The cluster diameter grows from 58 A at 72 minutes to 106 A at 350 minutes by a power function of time, $t^{0.37}$. On the other hand the particle size of the crystallite in the cluster grows from 48 A to 64 A according to the power law $t^{0.236}$ in the same time. From the data at 500 C, a power $n$ of 0.251 was evaluated. The power 1/4 suggests that the growth of the crystallite is driven by the surface mobility and thermal force in the present system.\(^\text{11}\) Although the scaling law does not hold in the initial stage, we extend the calculation of the cluster diameter as shown in Fig. 5. The cluster diameter at initial stage turned out to be comparable to the particle size of the crystallites, though the error of the cluster size might be bigger in the stage. One can still say that the new phase clusters are almost single crystal and increase in number but not in size at the early times ($t<10$ min.), then grow faster than the crystallites to the size of about twice that of the crystallites at 350 minutes.
CONCLUSIONS

X-ray diffraction has been utilized for the study of the crystal structure of alloys. Although X-ray source is relatively intense, it penetrates only into the surface of the specimen. While neutron can penetrate through the specimen, so that bulk properties of the specimen could be obtained. With high flux neutron and special neutron scattering devices, SANS and WAND at ORNL, bulk properties of spinodal decomposition of MnCu alloy was studied and time dependent growth of the cluster of the decomposed phase and the crystallites in the cluster was discussed.

Utilizing inelastic scattering of neutron, lattice instability of the bcc-based alloys was studied at JAERI to understand microscopic origin of the martensitic transformation which is directly related to the extraordinary mechanical properties such as shape memory effect, pseudo-elasticity and high damping property.

It is proved in these studies and will be proved in the future experiments that neutron is one of the best probes to explore the physical origin of the interesting solid state properties of alloys.

ACKNOWLEDGMENTS

The author express his sincere thanks to many co-workers of JAERI and ORNL specially to M. Iizumi, A. Nagasawa, B. D. Gaulin and S. Spooner for their stimulating discussions in the studies. Technical supports from Department of Physics and Reactor Division of JAERI and ORNL are also acknowledged.

REFERENCES

1. C. Zener; Phys. Rev. 71 (1947) 846
6. K. Oki, H. Sagana, and T. Eguchi; J. de Physique C7 (1977) 414
A SHORT NOTE ON EARLY OBSERVATIONS OF NEUTRON SCATTERING BY CRYSTALS

Ryukiti R. HASIGUTI

Faculty of Engineering
University of Tokyo
Professor Emeritus
Kakinoki-zaka, 2-23-10
Meguro-ku, Tokyo 152, Japan

ABSTRACT

In early 1940's we have performed experiments of neutron scattering by crystals making use of a simple Rn-Be neutron source. These were almost ten years earlier than the start of active neutron scattering experiments all over the world making use of nuclear fission reactors' more intense neutrons sources. I would describe here some examples of our early rather historically interesting experiments.

First of all I would like to thank the Session Chairman Dr. B. Dorner for adopting this proposed short comment, which I rather hesitated to present because this is not concerned with an advanced research, but is concerned with an old research of rather historical interest.

This morning, President S. Shimomura remarked in his Opening Address that the experimental researches of neutrons as microscopic probes were actively started in 1950's all over the world making use of nuclear fission reactors as intense neutron sources. But our studies of neutron scattering were started ten years before them, i.e. in early 1940's¹. That was fifty years ago from now.

As we could not use nuclear reactors at that time, we, Prof. Motoharu Kimura and myself, used a radon-beryllium neutron source. This is, so to say, to take photographic pictures in the moonlight instead of taking pictures in the sunshine. Nevertheless, we could obtain the neutron scattering results in the moonlight. The thermal neutrons from a paraffin howitzer with 200-300 mC Rn-Be source were detected by a BC₃ ionization chamber and a linear amplifier. About 2,000 counts per minute were obtained without a scatterer, and the residual counts due to
higher energy neutrons above Cd cut-off were 5% or less.

The items we studied by neutron scattering were, for example, (1) Variation in total cross section of metals such as iron, copper and alu-
mum by cold-working \(^{1\text{)}2\text{)}3\text{)}\), in which the primary extinction effects
were observed in annealed iron and copper, but were not observed in alu-
mum presumably because of the smallness of mosaic blocks in aluminum.

(2) The effect of thermal strain in the diffractive scattering of neu-
trons by quartz \(^{4\text{)}5\text{)}\), in which the reduction of the primary and the sec-
ondary extinction effects due to the thermal strain was observed, (3)
Neutron scattering cross sections by order-disorder Ni-Fe alloys\(^{6\text{)}\)}, and
(4) Some other items including phase transitions such as precipita-
tions in metallic alloys and so on.

All of the above experiments were performed at Late Professor S.
Nishikawa's Laboratory of the Institute of Physical and Chemical Re-
search (RIKEN). Prof. M. Kimura, my senior coauthor, now Prof. Emeritus
of Tohoku University, was a regular scientist at IPCR, while I was a
part-time scientist there because I was affiliated with other institue
(Imperial Research Institute for Aeronautics) at that time.

ACKNOWLEDGMENT

Finally, I would like to thank the Japan Atomic Energy Research
Institute for giving me to present at the Symposium of Advanced Nuclear
Research of Neutrons as Microscopic Probes this early work of historical
interest performed by Prof. M. Kimura and myself fifty years ago.

REFERENCES

   (1943), 495.
   (1943), 530.
POLYMER RESEARCH BY NEUTRON SCATTERING

D. Richter

Institut für Festkörperforschung
Forschungszentrum Jülich
D–5170 Jülich, Germany

ABSTRACT

Polymer physics aims on an understanding of the macroscopic behavior of polymer systems on the basis of their molecular structure and dynamics. For this purpose neutrons serve as a unique probe, allowing a simultaneous investigation of polymer structure and dynamics on a molecular scale. Furthermore, hydrogen deuterium exchange facilitates molecular labeling and offers the possibility to observe selected chains or chain parts in dense systems. Neutron small angle scattering reveals information on the conformation and possible aggregation of polymer chains. Data on linear and star like molecules are shown as examples. High resolution neutron spin–echo spectroscopy observes the molecular dynamics of long chain molecules. Results on the large scale motion of chains in polymer melts are presented. Finally, experiments on chain relaxation close to the glass transition are displayed. Three distinctly different relaxation processes are revealed.

INTRODUCTION

Macroscopic properties of polymeric matter like the mechanical behavior: the moduli, the strength, the viscoelasticity or transport properties and phase behavior are considered to be understood, if they are explained on the basis of molecular structure and dynamics. In order to fulfill this task, subtle probes are needed which are sensitive to the relevant molecular space and time regimes. Most important are scattering methods like X–ray and neutron scattering. Photons cover an extremely broad wavelength spectrum and are used both for structural and dynamic investigations. Unfortunately, however, the achievable time resolution which is associated with the photon energy and the spatial resolution, related to the wavelength, do not correspond. Thermal and cold neutrons, on the other hand, offer wavelengths in the molecular range and, at the same time, energies in the thermal region. This makes them a unique probe, allowing a simultaneous space–time observation of atomistic and molecular processes. Secondly, due to the nature of the scattering process occurring at the nuclei, isotop exchange facilitates atomistic labeling without strongly disturbing the chemical nature of the molecules. In particular, the different scattering properties of hydrogen and deuterium allow contrasting of organic substances. For example, only neutron scattering could access such basic properties as the chain dimension of a polymer in the bulk state.
STRUCTURAL INVESTIGATIONS

Medium and large scale structures are accessed by small neutron scattering (SANS). SANS machines are built on the principle of a pin hole camera. Neutron monochromatization is performed by a velocity selector. Thereafter, a collimation section prepares the appropriate divergence of the incoming beam. The scattered neutrons are counted with a multi detector, positioned in a flight tube at a variable distance from the sample. In this way, momentum transfers, down to about 10^{-3} \text{ Å}^{-1} are reached, covering a spatial range up to several thousand Å. The Bonse–Hart method, using the intrinsic width of Bragg reflections from perfect silicon crystals as resolution elements, extends this observation window into the range of microns. SANS today is one of the most widespread applications of neutron scattering. In the following two recent examples are given.

Temperature dependent chain dimension in polymer melts

Already the first SANS applications to polymer physics aimed on the evaluation of the polymer conformation in a melt \(^1\). Thus, it may be amazing that still substantial results may be obtained. Neutron scattering on a labeled chain in a polymer melt reveals the chain form factor, containing the chain conformation and, in particular, the chain dimension

\[
R_g^2 = \frac{1}{6} \phi \langle T \rangle \ell N
\]  

(1)

where \(R_g\) is the radius of gyration, \(C_m\) the characteristic ratio, \(\ell\) the main chain bond length and \(N\) the number of bonds along the chain. The most important and generally accepted model for the evaluation of polymer conformations, the rotational isomeric state model (RIS) by Flory \(^2\), calculates the chain conformation in the ideal state on the basis of local interactions between rotational isomers of different bonded states. Non bonded interactions are taken into account only locally. The characteristic ratio, \(C_m\), is thus only related to local interactions along the chain. The population of rotational isomeric states depends on temperature via the balance between entropy and energy. In general, with increasing temperature, a chain will shrink because more gauche states are occupied, allowing the chain to coil more. A precise measurement of the temperature dependence of \(R_g\), and thus of \(C_m\) (\(T\)) allows a detailed experimental access to this mechanisms.

Figure 1 presents SANS data from poly(ethylene–propylene) alternating copolymer (PEP), taken at different temperatures in form of a Zimm plot \(^3\). The Zimm plot takes advantage of the low Q expansion of the scattering function

\[
\frac{1}{S(Q)} = \frac{1}{\varphi(1-\varphi)V_w} \left( 1 + \frac{Q^2 R_g^2}{3} \right)
\]  

(2)

where \(S(Q)\) is the absolutely normalized scattering intensity, \(\varphi\) the polymer concentration, \(V_w\) the scattering volume. The decreasing slopes of the scattering curves in Figure 1 thus indicate the gradual reduction of the radius of gyration with increasing temperature. The upper part of Figure 2 displays the resulting temperature dependence of \(R_g\) for PEP \(^3\). Within the observation window, \(R_g\) decreases by about 10%, exhibiting a temperature coefficient \(\kappa = -1.16 \cdot 10^{-3} \text{ K}^{-1}\) in close agreement with the prediction of the RIS model \(\kappa = -1.1 \cdot 10^{-3} \text{ K}^{-1}\) and earlier results on θ solvents \(\kappa = 1 \cdot 10^{-3} \text{ K}^{-1}\). As a new feature, the SANS data reveal a gradual decrease of \(\kappa\) with increasing
Fig. 1: Zimm plot of the SANS data from the PEP sample at various temperatures.

Fig. 2: Experimental and theoretical results for the temperature dependence of the radius of gyration for polyethylene-propylene (a) and polypropylene (b). The dashed lines give predictions of the RIS model.

Fig. 3: Form factors for monodisperse polymer stars with functionalities between 8 and 64 (from below). The radius of gyration were obtained from the maximum in the Kratky plot.

Fig. 4: Structure factors for 18 arm stars solutions for some representative concentrations (● 19.2%; ▲ 14.6%; • 9.9%; ○ 7.4%; Δ 2.5%; * 1.5%; ♦ 1 %) For a better visualization the data are offset by an additive constant.
temperature. We emphasize the excellent quantitative agreement between RIS predictions and experimental results. Compared to earlier experiments using different Θ solvents, SANS on polymer melts has the advantage of a much larger temperature range, combined with the absence of specific solvent effects.

With this result and a similar experiment on polyethylene /4/ at hand, one could be satisfied and take the RIS model finally for granted. However, further experiments on polymers with higher side group density (polypropylene, (PP)) or larger side groups (polyethylene (PEE)) led to a pronounced disagreement with RIS predictions, which apparently cannot be reconciled /5/. As an example, the lower part of figure 2 presents the temperature dependent radius of gyration for atactic PP. As for isotactic PP /6/, the radius of gyration is practically independent of temperature. This result contrasts to Θ solvent data and disagrees to most of the RIS predictions. In particular, the independence on tacticity cannot be explained in terms of a RIS ansatz. Similar discrepancies are found for PEE. Obviously, more numerous or larger side groups cause severe difficulties for a description of Cm in terms of very local interactions, which is the basis of RIS.

Star polymers in solution

Star polymers consist of linear chains, connected at one central point and can be considered as prototype materials for branched polymers. They also have practical interest, for example, as viscosity modifiers in motor oils. Their conformation is described in analogy to semidilute polymer solution as a succession of spatially inhomogeneous blobs, growing from the center to the rim /7/. Progress in the technique of anionic polymerization allows the synthesis of monodisperse stars with functionalities up to f = 128. Figure 3 presents the forms factors of a series of stars with different functionalities (8 < f < 64) /8/. The scattering curves have been normalized to the monomer concentration. The Q scale was adjusted to the radius of gyration. While in the tails the scattering curves from all stars collapse to a single curve — here we observe the scattering from single arms, which is identical for all stars — at low Q with increasing functionality an increasingly important build-up of intensity is observed. This intensity increase originates from the coherent superposition of intensity from the different arms and, accordingly, is proportional to f.

Star polymers in dilute solution represent a very inhomogeneous monomer density distribution. Increasing the monomer concentration, therefore, leads to an important osmotic repulsion between different stars. Other than linear chains, which interpenetrate easily, star polymers exhibit ordering phenomena in the neighborhood of the overlap concentration φ*. Varying concentration and functionality, such ordering phenomena were investigated systematically on a series of stars /8,9/. The interstellar structure factor S(Q) was evaluated on the basis of

\[ S(Q) = \frac{I(Q)}{(\Phi V_n P_0(Q))} \]  

(3)

Thereby, I(Q) is the normalized intensity and P(Q) is the polymer form factor, which was taken from the low concentration extrapolation of the intensity. The thus obtained structure factors for an 18 arm polyisoprene star solution are shown in figure 4. From low to high concentration, we observe the gradual development of a peak structure which is maximal around \( \Phi \approx 10\% \) and diminishes towards higher concentration. (With \( \Phi^* = V_n/(4/3\pi R_g^2) \) we arrive at 10.1%). We note that S(Q) at high Q does not reach unity but levels off towards lower values. Most likely this is caused by a form factor, changing with concentration, which is not considered in equation 3. Figure 4 also shows that the position of the maximum in S(Q) increases with increasing concentration.
Comparing stars and linear polymers, in dilute solution the osmotic pressure in both cases is proportional to the number of molecules in solution. In the semidilute regime, where the branches of different stars or linear polymers, respectively, interpenetrate, we have a more or less uniform segment distribution. There, the osmotic pressure is given by the number of blobs in the system. \( \Pi \approx kT \xi(\Phi)^2 \), where \( \xi(\Phi) \) is the blob size. Around \( \Phi^* \), a transformation occurs from a state where, with respect to the osmotic pressure, all arms of one star act as one entity to another state where each arm does not know anymore to which star it belongs and acts separately. As a consequence, a sudden increase of the osmotic pressure is required. This extra osmotic pressure is the basis of the repulsion between polymer stars. Witten et al. \( /10/ \) have worked out a scaling theory and predict that a jump in the osmotic pressure should be proportional to \( f^{3/2} \). Accordingly, also the peak height in \( S(Q) \) should follow \( f^{3/2} \) scaling.

Figure 5 displays the structure factor \( S(Q) \) for the different stars at the overlap concentration \( \Phi^* \). In order to make them comparable, the structure factors were scaled such that in the high \( Q \) limit all \( S(Q) \) curves approach 1. Figure 5 demonstrates the build-up of structure in going to higher functionality. While for the \( f = 8 \) arm star, the peaks in the structure factor is barely developed, with increasing functionality the peak sharpens up and narrows. The insert in figure 5 displays the relative peak height \( S(Q_{\text{max}})/S(0) \) as a function of functionality. The solid line displays the predicted \( f^{3/2} \) behavior. Within experimental accuracy, the results at the lower functionalities follow the theoretical prediction well while the peak height for the 64 arm star is clearly larger, possibly an indication for macrocrystalline ordering. The formation of a macrocrystal at \( f = 64 \) is further evidenced by the observed two-dimensional intensity pattern. There, the peak shows itself in form of a concentric ring around the \( Q = 0 \) position. For a liquid, the intensity distribution along the ring should be homogeneous. In the case of the 64 arm star, bright spots at certain positions along the ring indicate preferred orientations or a grain structure in the sample which cannot possibly be caused by a liquid-like state. Further experiments will be necessary to get to the details of the macrocrystalline order.

**DYNAMIC EXPERIMENTS**

The interesting mechanical dynamical properties of polymer systems relate to the large scale motions of polymer chains. Observation of their space time evolution requires extremely high resolution neutron spectroscopy, operating at low angles. Neutron spin–echo spectroscopy (NSE) is well adapted to this task. Decoupling energy resolution and intensity, neutron spin–echo directly measures velocity differences of incoming and scattered neutrons in comparing the number of Larmor precessions of the neutron spin in magnetic guide fields before and after scattering. In this way, relative energy resolutions in the order of \( 10^{-5} \) may be achieved with an incoming wave length band of 20 % width. Presently, neutron spin–echo experiments are only available at the ILL in Grenoble and at the LLB in Saclay. Further neutron spin–echo spectrometers are being built in Germany and Japan. While NSE is the basic instrument for the investigation of polymer dynamics, time of flight methods are also of interest in order to reveal faster relaxation processes and soft phonons, which are in particular important in relation to the glassy behavior of polymer systems.

**Molecular dynamics in a polymer melt — direct observation of entanglement distances**

High molecular weight polymeric liquids exhibit unusual dynamic properties. Depending on the time scale of observation or temperature, the same polymer may
Fig. 5: Structure factors $S(Q)$ for stars with the functionalities $f = 8 \Delta$; $f = 18 \sigma$; $f = 32 \Delta$; and $f = 64 \sigma$. The structure factors are taken at the overlap concentration $\Phi^*$. The insert displays the ratio $S(Q_{\text{max}})/S(0)$ as a function of functionality.

Fig. 6: Characteristic frequency for the Rouse decay for different polyisoprene samples as a function of $Q$. The insert displays the scaling behavior of the dynamic structure factor if plotted versus the Rouse scaling variable $Q^2 \eta/\sqrt{Wt}$. The different symbols correspond to different $Q$ values. (The scale on the right side is offset by a factor of ten.)

Fig. 7: Dynamic structure factor from PEP, displayed in a scaling plot against the Rouse variable. $Q$ values from above (0.058 Å$^{-1}$; 0.068 Å$^{-1}$; 0.078 Å$^{-1}$; 0.097 Å$^{-1}$; 0.117 Å$^{-1}$; 0.135 Å$^{-1}$). The solid lines are the result of a fit with the Ronca model.

Fig. 8: Neutron spin–echo result from polybutadiene approaching the glass transition. The data are scaled with the viscosity time scale $\tau_\eta$. The solid line represents the master function obtained for the spectra at temperatures $T \geq 220$ K. The dashed lines are the result of fitting stretched exponentials to the different low $T$ spectra, keeping $\beta = 0.37$ fixed. • 280 K; • 260 K; △ 250 K; ◊ 240 K; × 230 K; □ 205 K; ▼ 190 K; ○ 180 K.
respond elastically, showing rubber like behavior or may flow like a liquid. This ambiguity in its mechanical properties is also also termed viscoelastic. The rubbery behavior which expresses itself by the the so-called plateau regime in the dynamic modulus, is commonly attributed to the effect of entanglements. They are thought to stem from geometrical or topological constraints, mutually imposed by the interpenetrating chain molecules. Their molecular origin, however, is not well understood. The reptation theory of viscoelasticity /11/ bases on the further assumption that the geometrical constraints can be modeled by a tube confinement, surrounding a given chain. At intermediate times, the polymer dynamics are restricted to a curve linear motion along the tube. The tube diameter d, thereby, may be interpreted as a distance between entanglements.

If chains could intersect freely, the chain dynamics would be described as thermal motion, damped via a friction coefficient \( \zeta \). In this so-called Rouse model/11/, the diffusing chain segments perform a random walk on the random chain profile. This convolution of two random processes leads to a mean square segment displacement \( \langle r^2(t) \rangle = \frac{Q}{W} t \) with \( W = 3kT/\zeta \), being the Rouse rate. In Gaussian approximation, the dynamical correlation functions relate directly to the mean square segment displacement and scale with the universal Rouse variable \( u = Q \gamma W^2 t \). Their characteristic frequency depends on the fourth power of the momentum transfer.

The presence of an intermediate dynamic length scale, \( \lambda \), changes the scaling behavior of \( S(Q,t) \) and causes systematic Q dependent deviations from the Rouse scaling. In the frame work of reptation, de Gennes derived an explicit first order expression for \( S(Q,t) \) /12/

\[
S(Q,t)/S(Q) = 1 - \frac{Q^2 d^2}{36} + \frac{Q^2 d^2}{36} \exp\left(\frac{\lambda^2}{36}\right) \text{erfc}\left(\frac{\lambda}{d}\right)
\]

(4)

The important feature in equation 4 is the factor \( Q \cdot d \), which introduces the new length scale. Due to the tube constraints, \( S(Q,t) \), only partially decays to a certain Q dependent fraction. The remaining elastic part is a consequence of long living segment—segment correlations due to the tube confinement. This elastic part actually decays only for times longer than a terminal time, \( \gamma d \), after which the chain has lost its memory of the original tube. At short times, when a polymer segment does not yet realize the spatial constraint, Rouse behavior should prevail. Figure 6 displays characteristic frequencies, derived from the initial decay of NSE spectra obtained from polyisoprene melts at 200° C /13/. The solid lines represent the \( \Omega \propto Q^4 \) law. A similar result has recently been reported for PDMS /14/, where geometrical constraints are supposed to be even less pronounced than for polyisoprene. The inset in figure 6 demonstrates the scaling behavior of the experimental spectra which, according to the Rouse model, are required to collapse to one master curve if they are plotted in terms of the Rouse variable \( u \). The solid line displays the result of a joint fit to the Rouse structure factor, the only fit parameter being the Rouse rate. An excellent agreement with theoretical prediction is observed.

The effect of entanglement constraints on polymer dynamics in polymer melts has been investigated on polyethylene (PEB), polyethylene propylene (PEP) and polyisoprene (PI) /13,15,16/. The results for all polymers are displayed in table 1. Here we remark only on the data from PEP. Figure 7 presents the measured dynamic structure factor for PEP at 492 K in a scaling form. The data are characterized by common initial decay, signifying the Rouse regime and a consecutive Q dependent cross—over into a plateau, resulting from the presence of an intermediate dynamic length scale beyond which density fluctuations are strongly limited. The solid line represents the result of a fit with a model by Ronca /17/, dealing with the cross—over from Rouse to entanglement controlled dynamics. It allows a very satisfying description of the experimental data, reproducing the line shape, the resulting sharp cross—over, and the Q dependence.
Fig. 9: Arrhenius representation of the relaxation rate obtained from fitting stretched exponentials to the spectra from polybutadiene at different temperatures. The solid line displays the viscosity time scale. The dashed line indicates the Arrhenius behavior of the low temperature branch.

Fig. 10: Temperature dependence of normalized intensities for polybutadiene as a function of energy transfers as measured with time of flight spectroscopy. The elastic intensity has been subtracted. The spectra are normalized to $T = 100$ K. The dashed line gives the reference value $1$ — no intensity change. The solid line is a calculation of the expected intensity increase, resulting from the Bose–Einstein occupation factor and the extrapolated low temperature Debye–Waller factor. The width of the vertical line marks the instrumental elastic resolution.

Table 1: NSE results on polymer melts

<table>
<thead>
<tr>
<th>Sample</th>
<th>T[K]</th>
<th>d[Å]</th>
<th>$10^9(\text{dyn} / \text{cm}^2)$</th>
<th>$r_c[\text{ns}]$</th>
<th>d[Å]</th>
<th>$10^9(\text{dyn} / \text{cm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI 1</td>
<td>468</td>
<td>52±1</td>
<td>4.4±0.3</td>
<td>-</td>
<td>52±1</td>
<td>4.4±0.3</td>
</tr>
<tr>
<td>PI 2</td>
<td>473</td>
<td>52±1</td>
<td>5.2±0.3</td>
<td>25</td>
<td>52±1</td>
<td>4.4±0.3</td>
</tr>
<tr>
<td>PEP homopolymer</td>
<td>492</td>
<td>47.5±0.4</td>
<td>3.1±0.1</td>
<td>15</td>
<td>43.5±2</td>
<td>0.3(448K)</td>
</tr>
<tr>
<td>PEP triblock</td>
<td>491</td>
<td>47.1±0.7</td>
<td>2.4±0.2</td>
<td>15</td>
<td>43.5±2</td>
<td>0.3(448K)</td>
</tr>
<tr>
<td>PEB-2</td>
<td>509</td>
<td>43.5±0.7</td>
<td>0.4±0.04</td>
<td>5</td>
<td>35(373K)</td>
<td>0.3(448K)</td>
</tr>
</tbody>
</table>
of the plateau levels. In order to compare with rheology, rheological data for the plateau modulus were converted into tube diameters using the reptation model /11/. They are included in table 1. In all cases the microscopically determined entanglement distances agree well with those obtained from rheology using the reptation concept.

Polymer motion near the glass transition

While the previous section dealt with large scale motion, here we are interested in the very local dynamics, i.e., the elementary motional processes. I present data on cis–trans–vinyl (46:47:7)polybutadiene (PB), (CD₂CD₃=CD₂CD₂)ₙ. This polymer consists essentially of a backbone only. The randomness of the chain structure is related to the random distribution of the two stable C bond orientations (cis and trans) relative to the double bond. Diffraction experiments reveal a static structure factor with a first peak due to interchain correlations around $Q = 1.5 \, \text{Å}^{-1}$, followed by a minimum around 2 Å⁻¹.

Figure 8 displays a set of NSE spectra, taken close to the first minimum of the structure factor /18/. The NSE spectra reveal a strongly stretched exponential relaxation $\exp\left(-t/\tau\right)^\beta$ with $\beta - 0.4$. Spectra taken at different temperatures have been rescaled on the basis of the time scale, $\tau_\eta$, set by the viscosity. At temperatures above 220 K, all experimental data collapse to a single master curve. At lower temperatures the rescaled spectra depart distinctly from such a behavior. Thus, above 220 K the dynamics at the level of interchain distances scale directly with the time scale, set by macroscopic viscosity. The freezing of all polymer relaxation modes from the slowest mode which dominates viscosity, to the fastest modes which are observed in the spin—echo experiments, follow the same time scale $\tau_\eta$. This result is by no means trivial and recently has become the subject of theoretical debate. Thus, above 220 K, NSE observes the structural relaxation or $\alpha$ relaxation, which completely dominates the dynamics. We note that the amplitude or spectral contribution of this relaxational process apparently stays constant. The master curve for all relaxation spectra extrapolates to 0.77 for $t \rightarrow 0$. Consequently, an important part of the spectrum decays outside the observation window of the spin—echo spectrometer.

Below 220 K the microscopic relaxation does not slow down as much as the viscosity. A single universal time scale for all length scales is no longer valid. We note that also the spectral contribution of the observed relaxation process starts to increase below 220 K. Figure 9 displays the observed relaxation rates in term of an Arrhenius diagram. The solid line, thereby, represents the temperature dependent viscosity time scale $\tau_\eta$. While above 220 K the good agreement between microscopic rates and $\tau_\eta$ is evident, below 220 K a strong decoupling of both scales is obvious. The relaxational process observed at low temperature reveals strong similarities to $\beta$ relaxation processes as observed with dielectric spectroscopy in other materials.

We now turn to the question of the missing intensity in the NSE spectra, indicating a second relaxation step at higher frequency. Figure 10 /19/ displays the results of time of flight experiments where the elastic scattering contribution was subtracted. At large energy transfers ($E > 3$ meV), the experiment observes harmonic phonons obeying Bose statistics (solid lines). Additional intensity is observed around 2 meV which increases strongly for temperatures above $T_g$. This intensity is the spectral contribution giving rise to the gap in the NSE spectra and constitutes a third fast relaxational process which seems to be characteristic for glass forming systems and has been observed in glass formers as different as ionic glasses, molecular glasses and polymers. These fast relaxation processes may be related to the soft phonon modes, which appear to be characteristic for the glassy state.

In summary, approaching the glass transition, the main chain polymer polybutadiene exhibits three distinctly different relaxation processes. (1) The structural or $\alpha$
relaxation dominates above 220 K all relaxation processes from viscosity to microscopic relaxation. (ii) Below 220 K the microscopic relaxation decouples from the viscosity time scale. At this temperature the spectral contribution of the microscopic relaxation shows a cusp–like behavior /20/. In a polymer without side groups this relaxation must relate to main chain motions and may be understood as a frustrated α relaxation which does not contribute anymore to macroscopic flow. (iii) In addition, a fast relaxational process is observed which is characterized by nearly constant relaxation rate and a rapidly increasing intensity above \( T_c \).

**RESUME**

Neutron scattering has proven to be a unique probe for the investigation of soft matter in particular polymers. This is mainly due to the possibility of contrast variation by hydrogen–deuterium exchange and the capability of a simultaneous investigation in space and time. For structural investigation with medium resolution, neutron small angle scattering today is the standard method governing the field. Access to the relevant large scale slow dynamic processes is obtained by neutron spin–echo spectroscopy. Other than in the case of SANS where ample possibilities exist worldwide, the NSE method still has to spread in order to cover the demand.

**REFERENCES**

SANS STUDIES OF SPACE-TIME ORGANIZATION OF STRUCTURE IN POLYMER BLENDS

†Takeji HASHIMOTO, ‡Hiroshi JINNAI, §Hirokazu HASEGAWA and ‡Charles C. HAN

†Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan
‡Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, U.S.A.

ABSTRACT

Self-organization of structure in polymer blends via spinodal decomposition (SD) was studied over a wide spatial-scale and time-scale (both being covered over 4 orders of magnitude) by using a combined time-resolved small-angle neutron scattering and light scattering method. The system studied was a binary critical fluids of deuterated polybutadiene and protonated polyisoprene having a narrow molecular weight distribution in a weak segregation limit. The scattering analyses made it possible to study space-time organization of various elements of the structures: (i) global structure, (ii) interfacial structure such as mean curvature of the tangled interface, interfacial area density, and interfacial thickness, (iii) "interphase", i.e., interfacial region with characteristic thermal concentration fluctuations, and (iv) the local structure characterized by the thermal concentration fluctuations within each domain. In the late stage SD, the form factor from the "interphase" was found to be time-independent, having the q-dependence of q^-2.5.

I. INTRODUCTION

The dynamics and pattern formation in systems undergoing spinodal decomposition (SD) are the subject of many theoretical and experimental investigation in the field of simple fluid mixtures, metallic alloys, inorganic glasses and polymer alloys.1)3) This problem concerning dynamical evolution of self-organized structure provides a fascinating example of nonlinear, nonequilibrium phenomena, exploration of which is an important theme in modern science.

In this work we used a polymer blend as a model system to study such phenomena as described above. An advantage using macromolecules comes from their unique features such that they have a very large microscopic length \( \xi_0 \) and a very long microscopic time \( t_0 \). These features are believed to facilitate experimental investigation of the nonequilibrium, nonlinear phenomena regarding the structure self-assembly to such a level that may be unattainable for small molecule or atomic systems. For typical polymers having degree of polymerization \( N \approx 10^4 \), \( t_0 \) is estimated to be \( 10^{12} \) times longer than that of small molecules (based upon Gaussian chain statistics)4) and \( \xi_0 \) to be \( 10^{10} \) times larger than that of small molecules (based upon reptation dynamics).5)6)

We investigate a binary critical mixture of amorphous polymers far above their glass transition temperatures so that the mixture is liquid like in a long time limit. Our mixture composed of DPB (deuterated polybutadiene) and HPI (protonated polyisoprene) has an inverted or LCST (lower critical solution temperature) type phase diagram whose theoretical
coexistence curve is shown in Fig. 1(a). We quench our mixture at an equilibrium state I in a single phase state to a state $I'$ inside the spinodal phase boundary. The mixture is thermodynamically unstable at $I'$, and hence the concentration fluctuations grow with time, generating the domains rich in one component A (e.g., DPB) and those rich in the other component B (e.g., HPI). The composition difference $\Delta \Phi(t)$ of the component A in between the two domains increases with time and reach equilibrium value $\Delta \Phi^e$ in the late stage where the size of the domains still increases and interfacial area keeps decreasing. The equilibrium state $F$ at the phase separation temperature $T$ is composed of the two macrophases 1 and 2 having $\phi_A$ equal to $\phi_{A1}^e$ and $\phi_{A2}^e$. This is an ordering process in which the free energy density $f$ of the system drops from $I'$ to $F$ as shown in Fig. 1(b) where the curve indicates $f$ as a function of $\phi_A$ at $T$ and the straight line indicates a common tangent at the points 1 and 2 on the curve having $\phi_{A1}^e$ and $\phi_{A2}^e$, respectively.

![Figure 1.](image)

Figure 1. (a) Coexistence curve for the DPB/HPI mixture calculated on the basis of Flory-Huggins theory, and (b) the composition dependence of the free energy density of the mixture at phase separation temperature 40°C. The component A is referred to DPB.

We are interested in studying the self-assembling process, mechanism and dynamics involved by this phase transition from state I to state F by using combined time-resolved small-angle neutron scattering (SANS) and light scattering (LS) technique. The technique enables us to study space-time organization of the structure over a wide length scale $r$ from 1 nm to 10 nm (or wavenumber scale $q$ from $10^{-4}$ to $10^0$ nm$^{-1}$) and over a wide time scale from 1 to $10^4$ min., covering from the early-to-late stage SD. A basic time-evolution equation of the order parameter $\phi(r,t)$ (spatial concentration fluctuations of one component) in our system is given by a generalized time-dependent Ginzburg-Landau (TDGL) equation for binary fluids, which takes into account the hydrodynamic effect.

**II. METHODS**

We investigate the pattern formation in our self-organizing system through time change of elastic scattering intensity of neutron and light, $I(q,t)$, i.e., the intensity of the Fourier mode
of the fluctuations with wavenumber \( q \) at time \( t \) after onset of SD. Experimentally \( q \) is varied by changing magnitude of scattering vector \( q \).

\[
q = \frac{(4\pi / \lambda)}{\sin(\theta / 2)}
\]  

(1)

The detailed experimental set-up and conditions of SANS and LS will be described elsewhere.\(^7\)

DPB has weight-average degree of polymerization (DP) \( N_w = 1700 \) and heterogeneity index characterizing polydispersity in DP, \( N_w/N_n = 1.04 \), where \( N_n \) is number-average DP. HPI has \( N_w = 2000 \) and \( N_w/N_n = 1.04 \). We investigated a critical mixture of DPB and HPI having a composition \( 47/53 \) vol/vol. Here we report our result at \( T = 40^\circ \)C. SANS studies in single phase state allowed us to determine the following characteristics of the mixture\(^7\): (i) it has an LCST phase diagram with spinodal temperature \( T_s = 36.1^\circ \)C which is well above the glass transition temperature \( T_g = -95^\circ \)C for DPB and \(-72^\circ \)C for HPI, (ii) the mean-field Flory interaction parameter per monomer \( \chi_{\text{eff}} \) was evaluated as a function of \( T \) and (iii) this result gives the parameter \( \varepsilon_T \) characterizing the thermodynamic driving force for the phase separation at a measuring temperature \( T = 40^\circ \)C,

\[
\varepsilon_T \equiv (\chi_{\text{eff}} - \chi_s) / \chi_s = 0.0668 \quad \text{(at 40°C)}.
\]  

(2)

The fact that \( \varepsilon_T \ll 1 \) indicates that our system is in a weak segregation limit. This situation is also confirmed later by a large characteristic interfacial thickness \( t_I \).

\[ t_I \equiv 7R_g \]

(3)

where \( R_g \) is the radius of gyration of DPB and HPI, separately estimated to be identical, 11.6 nm\(^7\), (iv) thermal correlation length \( \xi(T) \) was estimated and its value at 40°C is 25 nm.\(^7\) This value is larger than \( R_g \), reflecting again a weak segregation limit, and (v) \( \varepsilon_T = 0.0668 > 1/N (\approx 5 \times 10^{-4}) \) at \( T = 40^\circ \)C so that, the system is far outside the critical region as specified by the Ginzburg criterion. Thus the dynamical evolution of \( \phi(r,t) \) and \( I(q,t) \) should follow the mean-field behavior.

III. RESULTS

Figure 2 shows double logarithmically the scattering intensity profile \( I(q,t) \) as a function of \( q \) at various times after onset of SD. A part of the data at \( q \leq 10^{-2} \) nm\(^{-1} \) was obtained by LS and that at \( 2 \times 10^{-2} \leq q \leq 7 \times 10^{-1} \) nm\(^{-1} \) was obtained by using both 30 m and 8 m SANS instruments at NIST. The three sets of data cover a wide \( q \)-range of about four orders of magnitude. There is still a small gap in the \( q \)-range \( (10^{-2} \sim 2 \times 10^{-2} \text{ nm}^{-1}) \) which cannot be covered by our method. The wavenumbers corresponding to \( \xi^{-1} \) and \( R_g^{-1} \) are shown by the arrows for a reference. The lower half of the figure represents the time change of the profiles in the early-to-intermediate stage SD,\(^8\) while the upper half represents those in the late stage. The time scale covered is also about four orders of magnitude after the onset of SD, and the intensity scale extends over nine orders of magnitude.

We first focus our attention on the early-to-intermediate stage SD. After the onset of SD, a scattering maximum appears at the peak scattering vector \( q_m \approx 2 \times 10^{-2} \text{ nm}^{-1} \) in the \( q \)-range covered by the 30 m SANS instrument. The maximum intensity increases with time.
without a significant change in \( q_m \) up to about 10 min., then \( q_m \) rapidly shifts toward smaller \( q \), disappears in the \( q \)-gap, and appears again at the higher \( q \)-limit covered by LS. The solid curve shows the equilibrium scattering in the single phase state at 23°C before the temperature quench which was measured with 30m and 8 m SANS apparatus down to the lower \( q \)-limit of the 30 m instrument. The solid line below this \( q \) limit was estimated by best-fitting of the scattering function based on the RPA theory to the experimental SANS profile. The scattered intensity at \( q > 1/R_g \) decreases with time, reaching equilibrium value in the late stage at about 250 min for our system. This equilibrium scattering designated hereafter as \( I_{\text{thermal}}(q) \) corresponds to that from local, thermal concentration fluctuations occurring inside macroscopically phase-separated domains and is shown by the broken line. The intensity in the \( q \)-range lower than \( 10^{-1} \text{ nm}^{-1} \cong R_g^{-1} \) increases but the intensity in the \( q \)-range higher than \( R_g^{-1} \) decreases with time, resulting in the least change of the intensity in the \( q \) centered at \( R_g^{-1} \). The increase of the intensity is obviously due to the increase of the concentration fluctuations triggered by SD but the decrease of the intensity is turned out to originate from the same reason, as previously reported and as will be discuss briefly in sec. IV-5.

Figure 2. Time-resolved LS and SANS profiles after onset of SD. The upper and lower halves of the figure indicate, respectively, the profiles in the late stage and early-to-intermediate stage SD.

Next we discuss the time change of the profile in the late stage. It is very impressive and important to note that the scattering at high \( q \) as observed by SANS does not change much with
time, almost reaching equilibrium state, there being a very small decrease in intensity at \( q \leq \xi^{-1} (4 \times 10^{-2} \ \text{nm}^{-1}) \) but no change at \( q \geq \xi^{-1} \). This important feature has never been elucidated in the past. Here the small decrease in the intensity reflects a decrease of interfacial area density with time as will be discussed in sec. IV-3. On the contrary, the scattering at small \( q \) as observed by LS still changes with time. The time-independent part of the profile in \( \xi^{-1} \leq q \leq R_g^{-1} \) has an excess intensity (as highlighted by hatching) relative to that from the equilibrium intensity \( I_{\text{thermal}}(q) \) (broken line). This is also a very important result which has never been elucidated in earlier reports. We will discuss this scattering later in sec. IV-4.

Figure 3 highlights the scattering profile at a particular time in the late stage (at \( t = 1381.7 \ \text{min.} \) in which the intensity in the \( q \)-gap was interpolated by a broken line. We propose here that the profile can be classified into four regimes: (i) "GLOBAL" regime (\( q < 4.5 \times 10^{-3} \ \text{nm}^{-1} \)), (ii) "ASYMPTOTIC" (or "POROD") regime (\( 4.5 \times 10^{-3} < q < 2 \times 10^{-2} \ \text{nm}^{-1} \)), (iii) "INTERPHASE" regime (\( 2 \times 10^{-2} < q < 1 \times 10^{-1} \ \text{nm}^{-1} \)) and (iv) "LOCAL" regime (\( 1 \times 10^{-1} < q < 7 \times 10^{-1} \ \text{nm}^{-1} \)). The \( q \)-range for each regime is generally time-dependent, e.g., GLOBAL regime shifts toward smaller \( q \) with time but LOCAL regime is time-independent. ASYMPTOTIC and INTERPHASE regimes appear in the late stage. The former shifts toward smaller \( q \) with time, which appears to expand the \( q \)-range for INTERPHASE regime.

![Graph showing scattering profile](image)

**Figure 3.** LS and SANS profile at a particular time \( t = 1381.7 \ \text{min} \) in the late stage showing various \( q \)-regimes; Global, Asymptotic (or Porod), Interphase, and Local regimes.

### IV. ANALYSIS AND DISCUSSION

#### IV-1 Overall Feature

The time-change of the scattering function over the very wide \( q \) and \( t \) scales shown in Fig. 2 reveals one important conclusion as to the space-time organization of structure in our system: the structure having a shorter characteristic length \( r \) or higher wavenumber \( q \) relaxes toward equilibrium faster than that having a longer \( r \) or lower \( q \) (conclusion 1). This conclusion seems to be reasonable and universal too, because Fourier modes of the structures
having a higher $q$ have a higher gradient free energy $(\nabla \phi)^2 \sim q^2$ and hence relax faster toward a new equilibrium at the phase separation temperature. For our particular system, the structures as observed by SANS (with $q \geq 2 \times 10^{-2} \text{ nm}^{-1}$) essentially reached equilibrium in the late stage SD.

IV-2. Global Regime ($q < 1/R_m = H$)

Time-evolution of the global structure can be characterized by the time-changes in the wavenumber $q_m(t)$ and intensity $I_m(t)$ at the peak of the SANS or LS scattering function $I(q, t)$ and by the time-change in the shape of the scattering peak centered at $q = q_m(t)$. This is because $I(q, t)$ is given by

$$I(q, t) = \text{const.} \left(\Delta \phi(t)^2\right) q_m(t)^{-3} F(x), \quad x \equiv q/q_m(t).$$

(4)

$F(x)$ is the scaled structure factor which characterizes the shape of the structure self-organized. The characteristic wavenumber $q_m(t)$ is related to the characteristic length scale $L_m(t)$ of the global structure, $q_m(t) = 2\pi/L_m(t)$ and $I_m$ is related to $<\Delta \phi(t)^2>$, $q_m(t)$ and $F(x = 1)$.

Figure 4. Time changes of $q_m(t)$ and $I_m(t)$ in double logarithmic scale. $\tau$ is the reduced time. $t_{cr,1}$ and $t_{cr,2}$ are the crossover time between the intermediate and late stage and that between the late stage 1 and the late stage 2, respectively.

Figure 4 represents double logarithmically the time-changes of $q_m(t)$ and $I_m(t)$ as observed by SANS (at $t \leq 10 \text{ min}$.) and LS (at $t \geq 100 \text{ min}$). $\tau$ indicates reduced time, i.e., the real time $t$ renormalized by the characteristic time $t_c$ of the system. The value $q_m(t)$ decreases from about $2.5 \times 10^{-2} \text{ nm}^{-1}$, consistent with $3.0 \times 10^{-2} \text{ nm}^{-1}$ predicted from the linearized theory of SD by Cahn-Hilliard-Cook-deGennes-Pincus (conclusion 2), to $5 \times 10^{-4} \text{ nm}^{-1}$ over the four orders of magnitude of time covered in our experiment, corresponding to the
change in \( \Lambda_m(t) \) from about 200 nm to 12 mm. The dynamical exponents \( \alpha \) and \( \beta \) in the power-law analyses

\[
q_m(t) \sim t^{-\alpha}, \quad I_m(t) \sim t^{-\beta}
\]  

(5)

change with \( t \), e.g., from \( \alpha \approx 0 \) in the early stage, to 0.212, 1/3 in the intermediate stage and finally to 0.8 in the long time limit of our experiment. The exponent \( \alpha \) greater than 1/3 definitely indicates an important contribution of the hydrodynamic term to the dynamical evolution of the structure self-organized (conclusion 3), though our system did not reach yet the hydrodynamic limit (\( \alpha = 1 \)). The time \( t_{cr,1} \) denotes the crossover time from the intermediate stage (in which \( \beta > 3\alpha \)) to the late stage (in which \( \beta = 3\alpha \)),8 and the time \( t_{cr,2} \) is the crossover time from the late stage 1 and the late stage 2 18 as will be discussed in sec. IV-3.

![Figure 5. Scaled structure factor obtained from the LS profiles in the late stage. Note that \( H(t)/q_m(t) = 2 \), independently of time. \( H(t) \) is the mean absolute value of interface curvature.](image)

Figure 5 shows the scaled structure factor \( F(x) \) obtained from the LS profiles in the late stage SD. \( F(x) \) which includes SANS profiles also will be presented elsewhere.7 In the late stage, \( F(x) \) at \( x \leq 2 \) becomes independent of time, indicating that the global structure grows with dynamical self-similarity: the shape of the global structure is conserved and only the length scale \( \Lambda_m(t) = 2\pi/q_m(t) \) increases with time ("dynamical scaling").13 This \( F(x) \) is relevant to the structure factor for a bicontinuous domain structure.14 An asymptotic form of \( F(x) \) for \( x > 1 \) changes with \( x \) such that

\[
F(x) \sim x^3 \quad (\text{for } 1 < x \leq 2),
\]

(6)

and

\[
F(x) \sim x^4 \quad (\text{for } x \geq 2).
\]

(7)
This crossover reflects the spatial crossover at \( r = R_m \) or \( q = 1/R_m = H \) where \( R_m \) is the mean radius of interface curvature and \( H \) is the mean absolute value of the curvature (\( H = 1/R_m \)). At \( r > R_m \) or \( q < H \), the interface appears to be tangled, giving rise to eq. 6 but at \( r < R_m \) or \( q > H \), the interface appears to be flat, giving rise to eq. 7 (Porod's law). Here it is in order to note that the interface of our system is hyperboloidal, having negative gaussian curvature. The result shown in Fig. 5 implies that

\[
x_c \equiv H(t)/q_m(t) \equiv 2,
\]

the dynamical changes of \( H(t) \) and \( q_m(t) \) are self-similar, and their changes are also mutually similar, keeping the ratio about 2 independently of time (conclusion 4).

IV-3. Asymptotic Regime (\( H < q < t^{-1}_f \))

In the asymptotic regime, the scattering arises from the heterogeneities of the scattering length or refractive index at the interface, and the scattering function is given by an asymptotic form:

\[
I(q) = \left[ \pi X(1-X) \right]^{-1} \Sigma q^{-4} \exp(-\sigma^2 q^2)
\]

where

\[
\tilde{I}(q) = I(q)/\int_0^\infty q^2 I(q) dq.
\]

\( X \) is the volume fraction of one of the domains, \( \Sigma \) is the interfacial area density, and \( \sigma \) is the parameter associated with \( t_f \), \( t_f = (2\pi)^{1/2} \sigma \). Eq. 9 is the Porod's equation generalized for a two phase systems with a finite interface thickness.

The asymptotic form of eq. 9 was confirmed experimentally for the LS data in the late stage, from which \( \Sigma \) and \( t_f \) were evaluated as a function of time. In order to test eq. 9, the observed scattered intensity must be corrected for \( I_{\text{thermal}}(q) \), though the correction is very small, as judged from Figs. 2 and 3. It should be noted in Fig. 5 that \( F(x) \) at \( x \geq 2 \) has \( x^n \) or \( I(q) \) at \( q \geq H \) has \( q^{-n} \) with \( n > 4 \) if the ordinate scale is expanded. The fact that \( n > 4 \) and that the asymptotic form of eq. 9 is valid lead us to the following conclusions: the interface observed at the length scale \( r < t_f = R_m \) is flat but has a diffuse boundary, and the interface at a given time in the late stage does not have a characteristic of fractal surface (conclusion 5). If it has the fractal surface characteristic, the exponent \( n \) should satisfy \( 3 \leq n \leq 4 \).

Figure 6 shows time-changes of \( \Sigma(t) \), \( t_f(t) \) and \( \Sigma(t)/q_m(t) \) in the late stage estimated on the basis of eq. 9. \( \Sigma(t) \) decreases with time, which is quite natural, driven by the interfacial tension, and is given by a power law

\[
\Sigma(t) \sim t^{-\gamma}
\]

with \( \gamma \approx 0.8 \), so that time evolution of the interface has dynamical self-similarity, i.e., dynamically fractal (conclusion 6). A close observation indicates that \( \gamma \) is slightly larger than \( \alpha \) at \( t_{cr,1} < t < t_{cr,2} \) and \( \gamma = \alpha \) at \( t > t_{cr,2} \) as revealed from the time change of \( \Sigma/q_m \). The inequality \( \gamma > \alpha \) suggests that the local structure with a higher \( q \) (\( \equiv \Sigma \)) relaxes faster toward equilibrium than the global structure with a smaller \( q \) (\( \equiv q_m \)), consistent with conclusion 1.
The characteristic interface thickness in the late stage covered in our experiment tends to decrease with time from about 200 nm to the equilibrium value \( t_{le} \) of about 80 nm shown by the solid line at the same crossover time \( t_{cr,2} \) between the late stages 1 and 2 (conclusion 7a). The equilibrium value \( t_{le} \) is consistent with the value predicted by the Joanny-Leibler theory\(^{19}\) (conclusion 7b).

![Graphs (a) and (b) showing changes in \( \Sigma(t) \) and \( t_1(t) \) over time](image)

**Figure 6.** Time changes of \( \Sigma_0 \), \( \Sigma/q_m \) and \( t_1 \) obtained from the LS profiles in the asymptotic regime and in the late stage SD.

**IV-4. Interphase Regime (Rg < r < t_1 or 1/t_1 < q < 1/R_g)**

The scattering in this regime may reflect the concentration fluctuations occurring inside the interphase, i.e., the interfacial region of a finite thickness (\( t_{le} \equiv 7 R_g \)). Figures 2 and 3 indicate that the scattering from the interphase in the late stage reaches time-independent intensity level and this intensity level is definitely higher than \( I_{thermal}(q) \) as highlighted by hatching in Figs 2 and 3 (conclusion 8a). It definitely has a q-dependence smaller than q\(^{-4}\). The intensity \( I_c \) corrected for \( I_{thermal}(q) (I_c = 1 - I_{thermal}) \) seems to have

\[
I_c \sim q^{-2.5}
\]

which is surprisingly analogous to the scattering from the crumpled tethered membrane\(^{20}\) (conclusion 8b). This intriguing phenomenon has never been reported before in the self-organization process via SD and deserves future work.

**IV-5. Local Regime (r < R_g or q > 1/R_g)**

In this local regime, the length scale of observation is so small or the wavenumber scale of observation so high that the scattering depends only on the local composition \( \phi_A(t) \). This local composition increasingly deviates from the initial composition \( \phi_A^0 \) with time. This scattering \( I_{thermal}(q) \) from the local thermal concentration fluctuations inside each domain is given by

---

81
\[ I_{\text{thermal}}(q, t) \sim \langle \phi_A(t)[1 - \phi_A(t)] \rangle_{\text{space}} q^{-2} \]  \hspace{1cm} (13)\\

where \( \langle Y \rangle_{\text{space}} \) means an average of the quantity \( Y \) over all space. The time evolution of the composition difference \( \Delta \Phi(t) \) was estimated from that of \( I_{\text{thermal}}(q, t) \). The result indicated that \( \Delta \Phi(t) \) increases with \( t \) and reaches equilibrium value \( \Delta \Phi^e \) in the late stage (at \( t \geq t_{\text{cr,1}} \)), consistent with the result in Fig. 4 (conclusion 9a). The difference \( \delta \Delta \Phi \) as defined below was found to decay exponentially with time in the intermediate stage SD,

\[ \delta \Delta \Phi(t) \equiv \Delta \Phi^e - \Delta \Phi(t) \sim \exp(-t/\tau_{1}) \]  \hspace{1cm} (14)

with \( \tau_1 = 100 \) min. at \( T = 40^\circ\text{C} \), i.e., the manner of the system achieving equilibrium, driven by the interfacial tension, is described by the linear differential equation of \( \delta \Delta \Phi(t) \) with time \( t \) (conclusion 9b).

V. SUMMARY

A number of conclusions (conclusions 1 to 9) were elucidated on the space-time organization of the structures in binary critical mixtures via spinodal decomposition by using a polymer mixture as a model system. The self-organization of the structures was found to be characterized by at least three independent length scales; (i) \( \Lambda_m(t) = 1/q_m(t) \), the characteristic length scale for the global structure, (ii) \( \xi(t) \), the characteristic interface thickness and (iii) the thermal correlation length \( \xi \) within each phase-separated domain. The mean radius of the interface curvature \( R_m(t) \) was found to have a special relationship with \( \Lambda_m(t) \) (conclusion 4). As for time-sequences of various events in the self-organization, the following points are worth noting: (i) the local composition first reaches the equilibrium one at the phase separation temperature \( T \) at \( t = t_{\text{cr,1}} \), the crossover time between the intermediate stage and the late stage (conclusion 9a), (ii) the interfacial thickness subsequently reaches the equilibrium value \( t_{\text{cr,2}} \) at \( t = t_{\text{cr,2}} \) in the late stage (conclusion 7a), but (iii) the interfacial area density \( \Sigma(t) \) (the "local wavenumber") and the global wavenumber \( q_m(t) \) keep decreasing with \( t \) to reduce the interfacial free energy. In the early time in the late stage \( (t_{\text{cr,1}} \leq t \leq t_{\text{cr,2}}) \), \( \Sigma(t) \) relaxes faster than \( q_m(t) \), which is consistent with the general law found in the ordering process driven by the interfacial free energy (conclusion 1).

ACKNOWLEDGEMENT

The authors are grateful to Dr. J. Douglass, NIST, for his enlightening comments on the scattering from the interphase regime.

REFERENCES

9) K. Kawasaki, Progr. Theor. Phys. 57, 826 (1977); K. Kawasaki and T. Ohta, ibid., 59,
   42, 93 (1965).
    4425 (1977).
16) G. Porod, Koll. Z. 124, 83 (1951); ibid. 125, 51 (1952); ibid. 125, 108 (1952).
NEUTRON DIFFRACTION ON RANDOM SYSTEMS

H. Ohno

Material Innovation Laboratory
Department of Fuels and Materials Research
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11, Japan

ABSTRACT

Investigation of the three-dimensional structures of molten salts and glasses are essential for systematic understanding of physical properties of these materials. Neutron diffraction method with isotopic substitution is useful, but has limitation. Some topics on the structural analysis of molten salts and glasses were summarized. The effectiveness of the computer simulation with molecular dynamics method for these understanding was also presented.

INTRODUCTION

Materials such as glasses, molten salts and liquid metals have become more importance in the filed of nuclear engineering, solar and thermal energy, fuel cells and the related filed. The physical properties of these materials are closely related to their structures. It is essential to know the three dimensional arrangements of constituent atoms in these materials for the systematic understanding of the physical properties of these materials.

To investigate the structures, the radial distribution and correlation functions of constituent atom pairs should be known. Neutron diffraction is useful for the analysis of partial correlation function of constituent atom pairs.

In this paper, some typical structural analysis on molten salts and glasses with neutron and x-ray diffractions are presented. The computer simulation with molecular dynamics method is also applied for the analysis of pair distribution functions of the constituent atom pairs in molten alkali fluoroberyllates and PbO-SiO$_2$ glasses.

MOLTEN ALKALI HALIDES

Many works for the analysis of molten structures on simple alkali halides have been examined by neutron and x-ray diffraction methods and the structure of molten alkali halides near the melting points were summarized as follows [1-3].
(a) The nearest ionic distance $r_1^1$ in the liquid is smaller than that of the crystal $r_1^S$ at the melting points.

(b) The first coordination number $n_1^1$ decreases from 6 in the crystal to 4 ~ 5 at fusion. These values agree with the $n_1^1$ (act.) calculated from the next proportional relationship using the experimental values of the other quantities:

$$V_m^S/V_m^1=(r_1^S/r_1^1)^3 \cdot (n_1^1/n_1^S), \quad (1)$$

in which $V_m^S$ and $V_m^1$ are the volumes of solid and liquid at the melting point. This estimation of $n_1^1$ may produce reliable results owing to the fact that the ratio of the packing densities between NaCl and zinc blend type crystals is 6/3.9, which is approximately the same as the ratio 6/4 of their $n_1^S$.

(c) $n_1^1$ may be a little larger at the larger $r_c/r_a$ in each series of halides, and

(d) The second peaks in the smaller ionic radius ratio $r_c/r_a$ of 0.3 ~ 0.5 are sharp and definite and their maximum positions $r_2^1$ are near to $(1.52 ~ 1.56)r_1^1$. When $r_c/r_a$ is larger (0.7 ~ 1.0), the second peaks are much broader.

The above facts should be understood as follows. (a) and (b): The shorter $r_1^1$ will be expected in the low coordination number $n_1^1$ as the general rule from the crystal chemistry. (c): The crystal of the larger $r_c/r_a$ has already looser packing and does not need so much volume expansion in fusion, resulting in larger $n_1^1$. (d): $r_2^1$ of $1.52 ~ 1.56$ $r_1^1$ lie between the values of 1.61 $r_1$ in the NaCl type and 1.41 $r_1$ in the zinc blend type of distribution and corresponds to the value of $n_1^1=4.8 ~ 4.3$ suggested from Bernal's model of random system[39]. The following three are the most important factors which affect the liquid structure of the alkali halides. (1) the summation of the ionic radii of cation and anion, $r_c+r_a'$, (2) the radius ratio $r_c/r_a$ and (3) the deformation of ions due to the unsymmetrical local field. (3) is characteristics of liquid and is not observed in crystalline state. Furukawa et al. have already pointed out that factor (3) is important comparable with factor (2) by the analysis of volume change in fusion and activation energy of electrical conductivity at the melting point[2].

Recently, computer simulation by Monte Carlo(MC) and molecular dynamics(MD) has been applied to many molten alkali halides [4,5]. The interionic potentials based on the corresponding solid state are employed for the simulation and the thermodynamical and structural properties are reported to be in good agreement with those of experiments.

Neutron diffraction method with isotopic substitution has merit to get the partial structure factors and the results are able to compare directly with those of the computer simulation. The partial correlation functions of some molten salts, such as NaCl[6], KCl[7], CsCl[8], RbCl[9], AgCl[10] and CuCl[11] were obtained by this method. However, the accuracy of data on some molten salts seems to be insufficient.
Table 1 shows the radial distribution function (r.d.f.) characteristics for NaCl, KCl, CsCl and RbCl by neutron diffraction analysis with isotopic substitution. According to the results of neutron diffraction, the nearest neighbor distance of unlike ion pair in molten state was shorter than that in solid state and the coordination number n is about 6 which is close to the value of solid state. The coordination number and the average distance of like ion pair are also same with those of solid state. The results indicate that the local configuration of ions in molten state is similar to that in solid state. However, the large volume change such as 10~25% in fusion could not be explained by the structural model proposed by the analysis of neutron diffraction with isotopic substitution.

Table 1 r.d.f characteristics for NaCl[6],KCl[7],CsCl[7] and RbCl[9] by neutron diffraction analysis with isotopic substitution.

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>KCl</th>
<th>CsCl</th>
<th>RbCl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1148K</td>
<td>1073K</td>
<td>973K</td>
<td>1023K</td>
</tr>
<tr>
<td></td>
<td>300K</td>
<td>1049K</td>
<td>919K</td>
<td>300K</td>
</tr>
<tr>
<td>melt</td>
<td>solid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d_{min}</td>
<td>0.22</td>
<td>0.295</td>
<td>0.306</td>
<td>0.485</td>
</tr>
<tr>
<td>r_{max}</td>
<td>0.26</td>
<td>0.306</td>
<td>0.326</td>
<td>0.485</td>
</tr>
<tr>
<td>d_{max}</td>
<td></td>
<td>0.485</td>
<td>0.540</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>5.8</td>
<td>6.1</td>
<td>6.0</td>
<td>5.9</td>
</tr>
<tr>
<td>±1</td>
<td></td>
<td>6.0</td>
<td>6.0</td>
<td>6.9</td>
</tr>
<tr>
<td>++</td>
<td>±0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d_{min}</td>
<td>0.27</td>
<td>0.350</td>
<td>0.340</td>
<td>0.340</td>
</tr>
<tr>
<td>r_{max}</td>
<td>0.37</td>
<td>0.416</td>
<td>0.485</td>
<td>0.485</td>
</tr>
<tr>
<td>d_{max}</td>
<td></td>
<td>0.630</td>
<td>0.505</td>
<td>0.486</td>
</tr>
<tr>
<td>n</td>
<td>13.0</td>
<td>12.0</td>
<td>12.0</td>
<td>13.0</td>
</tr>
<tr>
<td>±5</td>
<td></td>
<td>12.0</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td>--</td>
<td>±0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d_{min}</td>
<td>0.30</td>
<td>0.340</td>
<td>0.340</td>
<td>0.340</td>
</tr>
<tr>
<td>r_{max}</td>
<td>0.38</td>
<td>0.416</td>
<td>0.482</td>
<td>0.482</td>
</tr>
<tr>
<td>d_{max}</td>
<td></td>
<td>0.630</td>
<td>0.505</td>
<td>0.480</td>
</tr>
<tr>
<td>n</td>
<td>13.0</td>
<td>12.0</td>
<td>12.3</td>
<td>14.0</td>
</tr>
<tr>
<td>±5</td>
<td></td>
<td>12.0</td>
<td>12.3</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Biggin et al.[12] have reexamined on molten NaCl by neutron diffraction with isotopic substitution. Figures 1 and 2 show the partial structure factors S_{ij}(Q) and partial distribution functions G_{ij}(r) for NaCl at 1148K. They have also compared the total intensity I^{coh}(Q) derived from the neutron scattering structure factors S(Q) with I^{coh}(Q) obtained by x-ray diffraction[13], and the degree of agreement is impressive.
Stable isotopes such as $^{35}$Cl, $^{37}$Cl, $^{6}$Li and $^{7}$Li are mainly used for the studies by the isotopic substitution method. Other possible isotopes are N($^{14}$N, $^{15}$N), S($^{32}$S, $^{34}$S), Se($^{76}$Se, $^{82}$Se), I($^{129}$I, $^{127}$I), K($^{39}$K, $^{41}$K), Cu($^{63}$Cu, $^{65}$Cu), Ca($^{40}$Ca, $^{44}$Ca), Ni($^{62}$Ni, $^{64}$Ni mixed with natural Ni) and Cr($^{53}$Cr, $^{53}$Cr mixed with natural Cr). The limitation to promote the neutron diffraction to get the information of pair distributions of the constituent atom pairs is that cost of isotopes are very expensive and the neutron diffraction experiments need relatively a large amount of the sample. To eliminate these limitation, the application of anomalous dispersion techniques with neutron and x-ray are attractive. As an example, fig.3 shows the energy dependence of the real and imaginary parts of the scattering length for $^{149}$Sm [14].

Fig.2 The partial correlation functions for molten NaCl [12].
A: Na-Na
B: Cl-Cl
C: Na-Cl

Fig.1 The partial structure factors of molten NaCl [12].

Fig.3 The real($b^0+b'$) and imaginary($b'$) parts of the neutron scattering length for $^{149}$Sm[14].
Anomalous dispersion experiments are also possible with x-ray based on the fact that near an absorption edge the x-ray form factor has both real and imaginary parts which are wave-length dependent.

\[ f(Q) = f^0(Q) + \Delta f(Q) + \Delta f''(Q). \]  

(2)

The utilization of anomalous dispersion to separate pair distribution functions has, however, only really become feasible with high intensity x-ray sources such as synchrotron radiation which allow the wavelength to be continuously varied to obtain the optimum values of \( \Delta f(Q) \) and \( \Delta f''(Q) \).

STRUCTURAL SIMILARITIES BETWEEN ALKALI-FLUOROBERYLLATES AND ALKALINE EARTH SILICATES

There are remarkable correspondences between the structural chemistry of alkali fluoro-beryllate melts and that of alkaline earth silicate melts. The following three pairs, (1) LiF-BeF₂ and MgO-SiO₂, (2) NaF-BeF₂ and CaO-SiO₂, and (3) KF-BeF₂ and BaO-SiO₂, have quantitatively the same values for ionic packing density, viscosity coefficient, and equivalent conductivity in the intermediate composition range and under the reduced absolute temperature scale[15]. The quantitative similarity of these physical properties in molten state will be due to that the ratio of ionic radius between constituent cation and anion is very close and the ionic ratio of Be²⁺ and F⁻ or Si⁴⁺ and O²⁻ (Be²⁺/F⁻ = 0.227; Si⁴⁺/O²⁻ = 0.29) is very close to the ideal ratio 0.25 of the tetrahedral arrangement. This indicates the structural analogy between these three pairs.

Neutron diffraction with isotopic substitution method will be accomplished to analyze detail pair correlation functions. However, it is impossible to get these information by neutron diffraction in this stage and computer simulation with molecular dynamics (MD) method is useful to get three dimensional information of structures of these melts. MD simulation was applied in molten states at corresponding temperature of the following three pairs[16], LiBeF₃(T=710K; reduced absolute temperature : T/Tₘ = 1.07, Tₘ = melting point) and MgSiO₃(T=1973K; T/Tₘ = 1.07), and NaBeF₃(T=743K; T/Tₘ = 1.15) and CaSiO₃(T=1973K; T/Tₘ = 1.09), and KBeF₃(T= 673K; T/Tₘ = 1.11) and BaSiO₃(T=2100K; T/Tₘ = 1.12).

Figure 4 shows the pair correlation functions \( G_{ij}(r) \) of the pairs F-F/O-O, Be-F/Si-O, Li-F/Mg-O, Be-Be/Si-Si, Be-Li/Si-Mg and Li-Li/Mg-Mg in the MD-calculated LiBeF₃ (T=710K; T/Tₘ = 1.07) and MgSiO₃ (T=1973K; T/Tₘ = 1.07). There is excellent agreement in peak shapes and positions in the \( G_{ij}(r) \) curves of the MD-simulated LiBeF₃ and MgSiO₃ melts. The same results were also obtained for following two pairs, NaBeF₃ (T= 743K; T/Tₘ = 1.15) and CaSiO₃(T=1973K; T/Tₘ = 1.09), and KBeF₃(T=673K; T/Tₘ = 1.11) and BaSiO₃ (T=2100K; T/Tₘ = 1.12). The distribution of coordination number \( N_{ij}(r) \) of the constituent pairs are also excellent agreement. The results suggest that materials in corresponding state are isostructure concerning the network topology and cation configuration. Qualitative
The similarity of the constituent species in these melts are shown in Table 2.

![Graph showing G(r) for LiBeF₃ and MgSiO₃ melts](image)

**Fig. 4** A comparison of the pair correlation functions $G_{ij}(r)$ for LiBeF₃ at 710K [T/Tₘ=1.07] and MgSiO₃ at 1973K[T/Tₘ=1.07] obtained from the MD simulation [16].

<table>
<thead>
<tr>
<th></th>
<th>LiBeF₃ (710K)</th>
<th>NaBeF₃ (743K)</th>
<th>KBeF₃ (673K)</th>
<th>NBF/Be</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeF₄⁻</td>
<td>monomer</td>
<td>1.69</td>
<td>15.60</td>
<td>2.33</td>
</tr>
<tr>
<td>Be₂F₇⁻³</td>
<td>dimer</td>
<td>19.19</td>
<td>24.75</td>
<td>19.81</td>
</tr>
<tr>
<td>BeF₃⁻</td>
<td>chain</td>
<td>38.31</td>
<td>35.95</td>
<td>39.15</td>
</tr>
<tr>
<td>Be₂F₅⁻</td>
<td>sheet</td>
<td>34.15</td>
<td>23.55</td>
<td>32.88</td>
</tr>
<tr>
<td>BeF₂²⁺</td>
<td>3D network</td>
<td>6.67</td>
<td>0.15</td>
<td>5.83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>MgSiO₃ (1973K)</th>
<th>CaSiO₃ (1973K)</th>
<th>BaSiO₃ (2100K)</th>
<th>NBO/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₄⁴⁻</td>
<td>monomer</td>
<td>2.89</td>
<td>11.80</td>
<td>2.73</td>
</tr>
<tr>
<td>Si₂O₇⁵⁻</td>
<td>dimer</td>
<td>17.38</td>
<td>30.59</td>
<td>14.02</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>chain</td>
<td>37.56</td>
<td>32.99</td>
<td>46.38</td>
</tr>
<tr>
<td>Si₂O₄²⁻</td>
<td>sheet</td>
<td>33.14</td>
<td>18.30</td>
<td>27.60</td>
</tr>
<tr>
<td>SiO₂⁰</td>
<td>3D network</td>
<td>9.02</td>
<td>6.94</td>
<td>9.27</td>
</tr>
</tbody>
</table>

3D: three dimension, NBF: number of bonding fluorine. NBO: number of bonding oxygen

### GLASSY PbO-SiO₂ SYSTEM

The structures of glassy PbO-SiO₂ system have been studied by both x-ray [17] and neutron[18] diffractions. Figures 5 and 6 show Qi(Q) and G(r) of glassy state in PbO-SiO₂ system (66.02 ~ 29.58 mol% PbO) by x-ray diffraction. The intensity of the 1st peak at r=0.160nm in G(r) increased with SiO₂ content and the peak corresponds to Si-O pair in SiO₄ tetrahedron. The 2nd peak in G(r) at around 0.23 ~ 0.26nm corresponds to the nearest-
neighbor Pb-O and O-O pairs in SiO$_4$ tetrahedron. There are two types of Pb-O bond and Pb-O distance with 0.23nm(PbO$_4$ pyramid type) is dominant at high PbO content more than 50 mol% PbO. The probability of long distant Pb-O bond with 0.26~0.28nm increases as increasing SiO$_2$ content. The results indicate that Pb-O bonds become more ionic with an increase of SiO$_2$ content, which is consistent with the analysis of chemical shifts of $^{207}$Pb with NMR by Levental et al. [19].

K. Yamada et al.[18] have been examined short range arrangement of lead silicate glasses (PbO)$_x$(SiO$_2$)$_{1-x}$ (0<x<0.66) with pulsed neutron scattering over a wide range of the scattering vector Q up to 300nm$^{-1}$. Contrary to the x-ray diffraction analysis, the contribution of O-O and Si-O pairs in r.d.f. is comparable to that of Pb-O pair and the observed r.d.f. is able to be separated to these three pairs clearly. The results indicate that the short range configuration can well be described with the tetrahedral chains containing the isolated monomeric or double tetrahedral rather than with the ring structures. There are two types of Pb-O bonds, which is the same result with that of x-ray diffraction analysis [17].

**Fig.5** Q$_i$Q curves of glass PbO-SiO$_2$ system [17], (a)PbO-34.0mol%SiO$_2$, (b)34.9, (c)49.6, (d)60.8, (e)62.1, (f)66.2 and (g) 70.4mol%SiO$_2$.

**Fig.6** Total correlation functions of glassy PbO-SiO$_2$ systems[17].
SUMMARY

The neutron diffraction with isotopic substitution is useful for understanding three dimensional arrangements of the constituent atoms in the random systems such as molten salts and glasses. However, this method has been applied only to simple system and limited isotopes. The reason is that the neutron diffraction needs a large amount of sample and the stable isotopes used for the neutron diffraction is expensive. Alternative methods are the use of anomalous scattering method with synchrotron radiation and the computer simulation with molecular dynamics method. Spectroscopic methods such as laser Raman spectroscopy are also effective to determine the species of ions in the melts and glasses.

As a result, neutron diffraction is powerful for the analysis of structures on random systems, but the combination with x-ray scattering, laser Raman spectroscopy and MD simulation is necessary for detail understanding of the structures of random systems.

REFERENCES

BIOLOGY WITH NEUTRON RADIATION

Giuseppe ZACCAI
Institut de Biologie Structurale and Institut Laue Langevin
41, Avenue des Martyrs
F-38027 Grenoble Cedex 1
France

ABSTRACT

Neutron diffraction, elastic and inelastic neutron scattering experiments provide important information on the structure, interactions and dynamics of biological molecules. This arises from the unique properties of the neutron and of its interaction with matter. Coherent and incoherent neutron scattering amplitudes and cross-sections are very different for H and D (deuterium). Deuterium labelling by chemical or biochemical methods and H2O-H2O exchange is the basis of high resolution crystallography experiments to locate functionally important H-atoms in protein molecules. It is also very important in low resolution crystallography and small angle scattering experiments to solve large complex structures, such as protein-nucleic acid complexes or biological membrane systems, by using contrast variation techniques. The energies of neutrons with a wavelength of the order of 1-10Å are similar to thermal energies and inelastic neutron scattering experiments have been done with different energy resolutions (≥ 1μeV) to characterise the functional dynamics of proteins in solution and in membranes.

INTRODUCTION

The contribution of neutrons to structural molecular biology has been reviewed at the last International Conference on Neutron Scattering in 1991).

The interesting properties of neutrons for biological studies include a choice of wavelength from below 1Å to more than 10Å, soft energies and negligible absorption in most matter, isotope effects, scattering amplitudes independent of atomic mass, the negative coherent amplitude of 1H and its large incoherent cross-section. These are all significant advantages for high and low spatial resolution experiments to which should be added the unique applications related to inelastic neutron scattering for the study of thermal motions in the microelectron volt to millielectron volt energy range.

Low absorption leads to high penetration and negligible radiation damage to samples and to easy-to-design sample containers for extremes of temperature or pressure. Neutrons are scattered by nuclei, contrary to X-rays that are scattered by electrons. The isotope effect is particularly useful because of the large difference between the coherent scattering amplitudes and also the incoherent cross-sections of H and (2H) D, which makes possible deuterium labelling studies. The negative scattering amplitude of 1H, results in a coherent scattering amplitude close to zero for the light water molecule; for the first time solution experiments could be done as if in a “vacuum”. The large incoherent cross-section of 1H makes energy analysis possible, even with the relatively low incident neutron fluxes available. The low incident flux can be compensated for somewhat by the use of longer wavelengths, large beam cross-sections, long collimation distances to obtain good angular resolution and larger samples.

There is useful and important information in structural molecular biology at different levels of resolution. Diffraction to atomic resolution can only be observed from well-ordered

--- 92 ---
crystals. Low resolution information from crystals can also provide information on disordered components in nucleic acid-protein or membrane protein complexes. Studies of macromolecular structure and interactions in solution can be performed to very low resolution.

Studies at High Resolution

Neutron diffraction is complementary to atomic resolution X-ray crystallography by providing information on the positions of H atoms in the structure\(^2\). An important point is that because of H-D labelling this can be done with neutrons with significantly lower resolution data than with X-rays. In practice, even with very high quality crystals, X-ray data are not adequate to locate the one electron of a H atom. Neutron diffraction H-D exchange studies have provided information on structural fluctuations in proteins and on enzyme catalysis by showing which groups are protonated under given conditions. Lehmann has used neutron crystallography to study macromolecular interactions between a protein and small solutes in the context of protein stabilisation\(^3\). For a neutron crystallographic study, a large crystal volume is required (a factor of 100 larger than for X-rays). Currently, new large wavelength band approaches (quasi-Laue methods) are under development for pulsed sources (Schoenborn, private communication) and steady state reactors (Lehmann, private communication) that should greatly reduce the requirement for large crystals and data collection times.

2-dimensional crystals are studied to atomic resolution by state of the art methods in electron microscopy and neutron diffraction. In electron microscopy, a single crystalline patch can be observed and three dimensional information obtained by tilting the sample. Bacteriorhodopsin (bR, a light driven proton pump) a membrane protein, has been studied by this method\(^4\). Neutron diffraction is a powerful complementary method because of H-D labelling. In the case of bR, the structural information from samples especially prepared to include deuterated atom groups has played an important and independent role in the interpretation of the electron density map\(^5\). By using model building approaches and deuterium labelling, it was possible to locate groups in projection by neutron diffraction with 7Å resolution data, at which resolution in electron microscopy only the broad alpha helix density is observed. Furthermore, the possibility of studying the sample by neutron diffraction under different conditions (of temperature, hydration, illumination...) and following protons by H-D exchange allowed structure-function experiments on bR\(^6\). The future prospects of similar neutron experiments are very good on other samples such as the light harvesting complex or rhodopsin for which two dimensional crystals are now available which may not diffract to very high resolution.

Dynamics

Neutron inelastic scattering methods, have been applied to study the dynamics of soluble proteins by Doster et al.\(^7\), and of bacteriorhodopsin in purple membrane. The results allowed correlations to be made between dynamics and function \(^8\). Since the incoherent cross section of hydrogen is analysed in inelastic scattering experiments, H-D exchange is also used but it is H that dominates the scattering and acts as a label and D is not observed. The full potential of inelastic scattering to study dynamics of biological significance has not yet been realized. Obvious extensions of the application are experiments on large complexes, using H-D exchange to focus on different parts of the structure. Inelastic neutron scattering experiments to study protein dynamics have been reviewed recently by Smith\(^9\).

Low Resolution

There is a natural neutron scattering density contrast between important components of
biological structures, proteins, lipids, nucleic acids, aqueous solutions, with the possibility of enhancing it by deuterium labelling. Long wavelength neutrons that, unlike soft X-rays, suffer from negligible absorption in the sample are also an advantage for low resolution studies.

**Low resolution in crystals of complexes.** There is complementarity between a high resolution X-ray study in which a component is "invisible" because of disorder (and that is also invisible at low resolution because of low contrast between that component and the solvent) and a neutron low resolution neutron study that brings it up by contrast variation. Examples are the location of detergent in crystals of membrane protein detergent complexes\(^\text{10}\) the location of the nucleic acid component in viruses and nucleosomes, aminoacyl-tRNA complexes with tRNA\(^\text{11}\), and the location of lipid bound to lipovitellin\(^\text{12}\).

**Complexes in solution.** A number of functional protein nucleic acid complexes associated with protein synthesis have been studied by neutron scattering. Early work on tRNA, its solvent interactions and its interactions with amino-acid tRNA synthetases and polypeptide elongation factor have been reviewed\(^\text{11}\).

Multicomponent complexes can be studied by specific deuteration and label triangulation. The positions of all the proteins in the 30S subunit of the E. coli ribosome have been derived in this way\(^\text{13}\) and work on the 50S subunit is in progress\(^\text{14}\). The subunit arrangement of the HIV reverse transcriptase has also been deduced by this method\(^\text{15}\). If a complex can be "built" up sequentially, the mutual arrangement of components could be calculated from a neutron experiment without using isotope labelling. This could be a very powerful approach when complementary biochemical information is available on the structure of the components, e.g. the work of Arlaud, on complement proteins\(^\text{16}\). Baron et al.\(^\text{17}\) suggested a strategy to tackle multidomain protein structures by analysing small model domains at high resolution by NMR and putting them together from the low resolution analysis of the complex, for example by solution scattering methods.

The study of an interacting functional system in solution has recently become possible because of progress in molecular biology techniques. It is very rewarding when sufficient effort is put into the molecular biology and biochemical aspects involved. An excellent example is found in the work on RNA polymerase\(^\text{18}\). This study is still in progress. By using deuterium labelling and DNA engineering in order to simultaneously fix a repressor and the polymerase on a DNA double strand, the spatial arrangement between the different components is studied at well-defined steps in the function of the enzyme. A similar approach will be used to study the interaction of HIV reverse transcriptase with RNA\(^\text{15}\).

**New neutron methods** for low resolution studies are still being developed. Examples are spin contrast variation\(^\text{19}\) and the triple isotopic replacement method\(^\text{20}\) which could greatly enhance the information obtained from solution scattering experiments.

**Conclusion**

All of the above approaches have great potential for future scientific studies that, for success, depend mainly on sufficient investment of effort in sample preparation, in order to have a well-defined system and structural problem. The least effort required is for a solution study of a macromolecule, in which a milligramme of pure material could allow a very useful characterisation at the molecular level with a short experiment. At the other end of the scale, an experiment on an interacting system involving specific deuterium labelling is likely to require a very sophisticated effort in molecular biology and biochemistry.

**References**

[17] Barron et al. TIBS 16 (1990) 13-17
FUNDAMENTAL RESEARCH WITH NEUTRON INTERFEROMETRY

Helmut RAUCH

Atominstitut der Österreichischen Universitäten
Schützelstrasse 115, A-1020 Wien, Austria

ABSTRACT

The invention of neutron interferometry in 1974 stimulated many experiments related to the wave-particle dualism of quantum mechanics. Widely separated coherent beams can be produced within a perfect crystal interferometer which can be influenced by nuclear, magnetic and gravitational interaction. High order interferences have been observed connected with the occurrence of an interferometric spectral modeling. This effect has been demonstrated by a proper post-selection procedure showing a persisting action of plane wave components outside the wave packets. The verification of the \(4\pi\)-symmetry of spinor wave functions and of the spin superposition law at a macroscopic scale and the observation of gravitational effects including the Sagnac effect have been widely debated in literature. The coupling of the neutron magnetic moment to resonator coils permitted the coherent energy exchange between the neutron quantum system and the macroscopic resonator. This phenomenon provided the basis for the observation of the magnetic Josephson effect with an energy sensitivity of \(10^{-19}\) eV. Partial beam path detection experiments are in close connection with the development of quantum mechanical measurement theory. The very high sensitivity of neutron interferometry may be used in future for new fundamental-, solid-state and nuclear-physics application. Further steps towards advanced neutron quantum optical methods are envisaged.

INTRODUCTION

Different kinds of neutron interferometers have been tested in the past. The slit interferometer is based on wavefront division and provides long beam paths but only a very small beam separation\(^{1,2}\). The perfect crystal interferometer\(^{3,4}\) is based on amplitude division. The interferometer based on grating diffraction is a more recent development and has its main application for very slow neutrons\(^{5}\). A schematical comparison is shown in Fig.1. The perfect crystal interferometer provides highest intensity and highest flexibility for beam handling and is now most frequently used due to its wide beam separation and its universal availability for fundamental-, nuclear- and solid-state physics research.

The perfect crystal interferometer represents a macroscopic quantum device with characteristic dimensions of several centimeters. The basis for this kind of neutron interferometry is provided by the undisturbed arrange-
Figure 1: Scheme of a slit-, a perfect-crystal and a grating interferometer

ment of atoms in a monolithic perfect silicon crystal\(^3,6\)). An incident beam is split coherently at the first crystal plate, reflected at the middle plate and coherently superposed at the third plate (Fig.1b). From general symmetry considerations follows immediately that the wave functions in both beam paths, which compose the beam in the forward direction behind the interferometer, are equal \((\psi^I = \psi^{II})\), because they are transmitted-reflected-reflected (TRR) and reflected-reflected-transmitted (RRT), respectively. The de Broglie wavelength of the neutrons diffracted from such crystals is about 1.8 Å and their energy is about 0.025 eV. The theoretical treatment of the diffraction process from the perfect crystal is based on the dynamical diffraction theory, which can also be found in the literature for the neutron case\(^7-10\)). Inside the perfect crystal two wave fields are excited when the incident beam fulfills the Bragg condition, one of them having its nodes at the position of the atoms and the other in between them. Therefore, their wave vectors are slightly different \((k_1 - k_2 = 10^{-5} k_1)\) and due to mutual interference processes, a rather complicated interference pattern is built up, which changes substantially over a characteristic length \(\lambda_0\) - the so-called Pendellösung length, which is of the order of 50 μm for an ordinary silicon reflection. To preserve the interference properties over the length of the interferometer, the dimensions of the monolithic system have to be accurate on a scale comparable to this quantity. The whole interferometer crystal has to be placed on a stable goniometer table under conditions avoiding temperature gradients and vibrations.

A phase shift between the two coherent beams can be produced by nuclear, magnetic or gravitational interactions. In the first case, the phase shift is most easily calculated using the index of refraction\(^11,12\)):

\[
n = \frac{k_{in}}{k_0} = 1 - \lambda^2 N \sqrt{\frac{k_c^2 - (\frac{\sigma_1}{2})^2 + i \frac{\sigma_N \lambda}{4\pi}}} \tag{1.1}
\]

which simplifies for weakly absorbing materials \((\sigma_r \to 0)\) to

\[
n = 1 - \lambda^2 \frac{N b_c}{2\pi} \tag{1.2}
\]

where \(b_c\) is the coherent scattering length and \(N\) is the particle density of the phase shifting material. The different \(k\)-vector inside the phase shifter causes a spatial shift \(\lambda\) of the wave packet which depends on the orientation of the sample surface.
\[ A = \frac{(K - K_0)}{k} D_0 \quad \text{with} \quad K - K_0 = \frac{(1-n) \hat{k} \hat{s}}{(k \cdot \hat{s})} \quad (1.3) \]

As in ordinary light optics the change of the wave function is obtained as follows:

\[ \psi \rightarrow \psi_0 e^{iA \cdot \hat{n}} = \psi_0 e^{-iNDc^\lambda D} = \psi_0 e^{i\chi}. \quad (1.4) \]

Therefore, the intensity behind the interferometer becomes

\[ I_0 = |\psi_0^I + \psi_0^{II}|^2 \propto (1 + \cos\chi) \quad (1.5) \]

The intensity of the beam in the deviated direction follows from particle conservation:

\[ I_0 + I_H = \text{const.} \quad (1.6) \]

Thus, the intensities behind the interferometer vary as a function of the thickness D of the phase shifter, the particle density N or the neutron wavelength \( \lambda \).

Any experimental device deviates from the idealized assumptions made by the theory: the perfect crystal can have slight deviations from its perfection, and its dimensions may vary slightly; the phase shifter contributes to imperfections by variations in its thickness and inhomogeneities; and even the neutron beam itself contributes to a deviation from the idealized situation because of its momentum spread \( \delta k \). Therefore, the experimental interference patterns have to be described by a generalized relation

\[ I \propto A + B \cos(\chi + \phi_0) \quad (1.7) \]

where A, B and \( \phi_0 \) are characteristic parameters of a certain set-up. It should be mentioned, however, that the idealized behaviour described by equation (1.5) can nearly be approached by a well balanced set-up\(^{13}\). The reduction of the contrast at high order results from the longitudinal coherence length which is determined by the momentum spread of the neutron beam \( (\Delta \lambda = \frac{2\pi \delta k}{\lambda})^{-1} \). This causes a change in the amplitude factor of equ. (1.7) as \( (B-B \exp{-\frac{\lambda_1 \delta k_i \hat{l}^2}{2}}) \). The wavelength dependence of \( \chi \) in equ. (1.4) disappears in a special sample position where the surface of the sample is oriented parallel to the reflecting planes and the path length through the interferometer becomes \( D_0/\sin\theta_B \) and, therefore, the phase shift \( \chi = -2d_{\lambda}^B \lambda NDcD_0 \) becomes independent of the wavelength. In this case the damping at high interference orders due to the wavelength spread does not appear as in the standard position. Related results of a recent experiment where the interference pattern in the 256th interference order have been measured in the dispersive and the nondispersive sample position are shown in Fig.2\(^{14}\). The much higher visibility of the interferences in the nondispersive sample arrangement is visible and is caused by the much smaller momentum spread perpendicular to the reflecting planes.

All the results of interferometric measurements, obtained up until now can be explained well in terms of the wave picture of quantum mechanics and the complementarity principle of standard quantum mechanics. Nevertheless,
one should bear in mind that the neutron also carries well defined particle properties, which have to be transferred through the interferometer. These properties are summarized in Table 1 together with a formulation in the wave picture. Both particle and wave properties are well established and therefore, neutrons seem to be a proper tool for testing quantum mechanics with massive particles, where the wave-particle dualism becomes obvious.

Table 1: Properties of the neutrons

Particle properties:

mass: \( m_0 = 1.6749543(86) \times 10^{-24} \) g
spin: \( s = \frac{1}{2} \) K
magnetic moment: \( \mu = -1.91304308(54) \) \( \mu_K \)
half live: \( T_{1/2} = 641(8) \) s
electric charge: \( q < 2.2 \times 10^{-20} \) e
electric dipol moment: \( d < 4.8 \times 10^{-25} \) e.cm
confinement radius: \( R = 0.7 \) fm
quark structure: \( n = u - d - d \)

Wave properties:

Compton wavelength: \( \lambda_c = h/mc = 1.32,10^{-13} \) cm
de Broglie wavelength: \( \lambda_B = h/mv = 1.10^{-8} \) cm
coherence length: \( \lambda_c = \lambda^2/\Delta \lambda = 1.10^{-6} \) cm
packet length: \( \lambda_p = v \Delta t = 1.10^{-6} \) cm
decay length: \( \lambda_d = v T_{1/2} = 2.10^{-8} \) cm
phase difference: \( 0 \leq \chi \leq 2\pi \)

*) values belong to thermal neutrons (\( \lambda_B = 1.8 \) A, \( v = 2 \times 200 \) m/s)
All neutron interferometric experiments pertain to the case of self-interference, where during a certain time interval, only one neutron is inside the interferometer, if at all. Usually, at that time the next neutron has not yet been born and is still contained in the uranium nuclei of the reactor fuel. Although there is no interaction between different neutrons, they have a certain common history within predetermined limits which are defined, e.g., by the neutron moderation process, by their movement along the neutron guide tubes, by the monochromator crystal and by the special interferometer set-up. Therefore, any real interferometer pattern contains single particle and ensemble properties together. In the following chapters typical experiments performed mainly by our group within the last 15 years will be presented. Time has come to switch from classical to quantum neutron optics.

STOCHASTIC VERSUS DETERMINISTIC ABSORPTION

A certain beam attenuation can be achieved either by a semi-transparent material or by a proper chopper system. The transmission probability in the first case is defined by the absorption cross section \( \sigma_a \) of the material \( \frac{I}{I_0} = \exp(-\sigma_a ND) \) and the change of the wave function is obtained directly from the complex index of refraction (equation 1.1):

\[
\psi \rightarrow \psi_0 e^{i(n-1)KD} = \psi_0 e^{i\chi} e^{-\sigma_a ND/2} = e^{i\chi} \sqrt{\alpha} \psi
\]

(2.1)

Therefore, the beam modulation behind the interferometer is obtained in the following form

\[
I_0 = |\psi_0^I + \psi_0^{II}|^2 = [(1+a) + 2\sqrt{\alpha} \cos \chi]
\]

(2.2)

On the other hand, the transmission probability of a chopper wheel or another shutter system is given by the open to closed ratio, \( a = \frac{t_{\text{open}}}{(t_{\text{open}} + t_{\text{closed}})} \), and one obtains after straightforward calculations

\[
I = [(1-a)|\psi_0^{II}|^2 + a|\psi_0^I + \psi_0^{II}|^2]
\]

\[
= [(1 + a) + 2a \cos \chi]
\]

(2.3)

i.e., the contrast of the interference pattern is proportional to \( \sqrt{\alpha} \), in the first case, and proportional to \( a \) in the second case, although the same number of neutrons are observed in both cases. The absorption represents a measuring process in both cases because a compound nucleus is produced with an excitation energy of several MeV, which is usually deexcited by capture gamma rays. These can easily be detected by different means.

Figure 3 shows the dependence of the normalized contrast of the measured interference pattern on the transmission probability\(^{15,16}\). The different contrast becomes especially obvious for low transmission probabilities where the interfering part of the interference pattern is distinctly larger than the transmission probability through the semi-transparent absorber sheet. The discrepancy diverges for \( a \to 0 \) but it has been shown that in this regime the variations of the transmission due to variations of the thickness or of the density of the absorber plate have to be taken into account which shifts the points below the \( \sqrt{\alpha} \)-curve\(^{18}\). This can most easily
Figure 3: Sketch of the experimental arrangement for absorber measurements (above). (a) stochastic absorption, (b) deterministic absorption, (c) attenuation by a transmission grating. Reduction of the contrast as a function of beam attenuation for different absorption methods (below)\textsuperscript{16,17}.

be understood if the variation of the beam attenuation due to variations of the thickness or density fluctuations is included $a = \bar{a} + \Delta a$, which yields after averaging

$$\sqrt{\Delta a} < \sqrt{\Delta \bar{a}}$$

indicating that the points fall below the $\sqrt{\Delta a}$-curve.

The region between the linear and the square root behaviour can be reached by very narrow chopper slits or by narrow transmission lattices, where one starts to loose information of through which individual slit the neutron went. This is exactly the region which shows the transition between a deterministic and a stochastic view and, therefore, it can be formulated by a Bell-like\textsuperscript{19,20} inequality

$$\sqrt{\Delta a} > x > a$$

The stochastic limit corresponds to the quantum limit when one does not know anymore through which individual slit the neutron went. Which situation exists depends how the slit widths $s$ compares to the coherence lengths $(\Delta k_i \sim (2\Delta k_i)^{-1})$ in the related direction. In case that the slit widths become smaller than the coherence lengths, the wave function behind the slits show distinct diffraction peaks which correspond to new quantum states ($n \neq 0$), which now do not overlap with the undisturbed reference beam. The creation of the new quantum states means that those labeled neutrons carry information about the chosen beam path and, therefore, do not contribute to the interference amplitude\textsuperscript{21}. A related experiment has been carried out by
rotating an absorption lattice around the beam axis where one changes from $l << \lambda$ (vertical slits) to $l >> \lambda$ (horizontal slits), Fig.4, because the coherence length parallel to the reflecting lattice vector is much larger than in any other directions. Thus, the attenuation factor $a$ has to be generalized including not only nuclear absorption and scattering processes but also lattice diffraction effects if they remove neutrons from the original phase space.

A very similar situation exists if a very fast chopper produces beam bursts (packet lengths) shorter than the coherence time $\Delta t_c = \Delta / v$. In this case, diffraction in time occurs which also removes neutrons out of the original phase space. This limit is very difficult to reach with a mechanical chopper but it can probably be tackled with a high frequency spin flipper.

**NEUTRON JOSEPHSON EFFECT**

This phenomenon is based on the dipol coupling of the magnetic moment $\vec{\mu}$ of the neutron to a magnetic field $\vec{B}$ ($\vec{H} = -\vec{\mu} \vec{B}$) which causes the famous $\pi$-symmetry of spinor wave functions, as measured in early neutron interferometer experiments\(^{22,23}\)). The change of the wave function reads as:

$$\psi = \psi_0 e^{-i(Ht/\hbar)} = \psi_0 e^{-i(\mu B t/\hbar)} = \psi_0 e^{-i\vec{\sigma} \cdot \vec{r}/2} = \psi(\alpha)$$

where $\vec{\sigma}$ represents a formal description of the Larmor rotation angle around the field $\vec{B}$ ($\alpha = (\mu B t/\hbar) \vec{r}$). This enabled also the realization of the spin superposition experiments where spin-up ($\uparrow$) and spin-down states ($\downarrow$) are superposed producing a final state perpendicular to both initial states\(^{24,25}\)). It is interesting to mention that in the case of spin reversal by means of a resonance flipper the spin term is accompanied by an energy exchange equal the Zeeman energy $\Delta E = 2 \mu B$. This provided the basis for the observation of a new quantum beat effect; the magnetic Josephson analog.

A double coil arrangement can be used for the observation of a new quantum beat effect. If the frequencies of the two coils are chosen to be slightly different, the energy transfer becomes different too ($\Delta E = \hbar (\omega_{r1} - \omega_{r2})$).
\( \omega_{r-2} \)). The frequency difference can be made very small, if high quality frequency generators are used for the field generation. The flipping efficiencies for both coils are always very close to unity (better than 0.99). Now, the wave functions change according to

\[
\psi = e^{i(\omega_{r1}t)} |+\rangle + e^{-i\lambda} e^{i(\omega_{r2}t)} |+\rangle
\]  

(3.2)

Therefore, the intensity behind the interferometer exhibit a typical quantum beat effect, given by

\[
I = 1 + \cos \lambda + (\omega_{r1} - \omega_{r2}) t
\]  

(3.3)

Thus, the intensity behind the interferometer oscillates between the forward and deviated beam without any apparent change inside the interferometer\(^{26}\). The time constant of this modulation can reach a macroscopic scale which is correlated to an uncertainty relation \( \Delta E \Delta t \leq \hbar / 2 \). Fig.5 shows the result of an experiment, where the periodicity of the intensity modulation, \( T = 2\pi / (\omega_{r1} - \omega_{r2}) \), amounts to \( T = (47.90 \pm 0.15) s \) caused by a frequency difference of about 0.02 Hz. This corresponds to a mean difference \( \Delta E \) of the energy transfer between the two beams, \( \Delta E = 8.6 \times 10^{-19} \text{ eV} \), and to an energy sensitivity of \( 2.7 \times 10^{-19} \text{ eV} \), which is better by many orders of magnitudes than that of other advanced spectroscopic methods. This high resolution is strongly decoupled from the monochromaticity of the neutron beam, which was \( \Delta E_B = 5.5 \times 10^{-4} \text{ eV} \) around a mean energy of the beam \( E_B = 0.023 \text{ eV} \) in this case. It should be mentioned, that the result can also be interpreted as being the effect of a slowly varying phase \( \Delta(t) \) between the two flipper fields, but the more physical description is based on the argument of a different energy transfer. The extremely high resolution may be used for fundamental, nuclear and solid state physics applications.

The quantum beat effect can also be interpreted as a magnetic Josephson effect analog. In this case, the phase difference is driven by the magnetic energy

\[
\frac{2}{\hbar} (\Delta_2 - \Delta_1) = \omega_{r2} - \omega_{r1} = \frac{1}{\hbar} 2 \mu B_0
\]  

(3.4)

Figure 5: Quantum beat effect observed when the frequencies of the two flipper coils differ by about 0.02 Hz around 71.89979 kHz\(^{26} \).
which yields the observed modulation (compare equ. 3.2)

$$I = (1 + \cos \Delta(t))$$  \hspace{1cm} (3.5)

where \(\Delta(t) = 2\mu B_0 t/\hbar\). This is analogous to the well-known Josephson-effect in superconducting tunnel junctions\(^{27}\), where the phase of the Cooper-pairs in both superconductors is related according to

$$\frac{d}{dt} (\phi_2 - \phi_1) = \frac{1}{\hbar} (E_2 - E_1) = \frac{1}{\hbar} 2eV$$  \hspace{1cm} (3.6)

which is driven by the electrical potential \(V\) between both superconductors.

**POSTSELECTION OF STATES**

In the course of several neutron interferometer experiments\(^{28}\),\(^{29}\) it has been established that smoothed out interference properties at high interference order can be restored even behind the interferometer when a proper spectral filtering is applied. This postselection of states demonstrates that narrow plane wave bands, which are components of the wave packet, remain interacting even in those cases where the wave packets do not overlap in space anymore due to a large phase shift applied to one of them. A phenomenon which appears especially for less monochromatic and less collimated beams in the same way as it has been described for optical experiments too\(^{30}\),\(^{31}\). The interference pattern follows from the superposition of the wave functions for both beam paths and depends on the relative phase shift \(\chi = \Delta.k\) and on the momentum width \(5k\) of the beam (equ. 1.4\(^{32}\))

$$I(\Delta) = \left[ 1 + e^{-\Delta.6k}^2/2 \cos(\Delta.k) \right].$$  \hspace{1cm} (4.1)

The damping factor \(e^{-\Delta.6k}^2/2\) can be interpreted as the real part of the mutual coherence function of the interfering beams. The spatially separated parts of the wave function can be interpreted as result of the quantum superposition of two macroscopically distinguishable states, that is, a Schrödinger-cat-like state\(^{33}\),\(^{34}\). The associated momentum distribution of the separated coherent wave packets is given by the Fourier-transform which exhibit at high interference order a marked spectral modulation determined by the spatial shift of the wave trains

$$I(k) = |a(k)|^2 \left[ 1 + \cos(\Delta.k) \right]$$  \hspace{1cm} (4.2)

where \(a(k)\) is the amplitude function of the wave packet centered around \(k_0\).

This behavior is shown in Fig.6 where a dimensionless quantity \(m = D/D_0\) (\(D_0 = K_0/\hbar D_0\) denotes the lambda-thickness) is used as a measure for the phase shift\(^{35}\). It should be mentioned that this modulation becomes more pronounced and structured for increasing phase shifts indicating that the disappearance of the interference pattern in ordinary space is compensated by the appearance of the spectral modulation effect in momentum space. Figure 6 also shows that an interferometric spectral narrowing can be achieved which has the characteristic features of a squeezing phenomenon where one conjugate quantity (\(ak\)) is below the related coherent-state value whereas the \(\Delta x\)-value is enlarged accordingly. The phenomenon of complete
Neutron interference experiments at high order. Experimental set-up (above), loss of contrast at high order (middle), spectral modification of the beam in forward (0) and in deviated direction (H)\textsuperscript{35}).

Beam modulation indicates that complete information exists at the place of beam superposition at the interferometer exit guiding neutrons with distinct momentum values into the forward or deviated beam, respectively. This formal and experimentally proven behavior can be interpreted as the persisting action of plane wave components (exp(ikr)) outside the wave packet

\[ \psi(r) = \int a(k) e^{ikr} \, dk \]  \hspace{1cm} (4.3)

and it shows that separation in ordinary space is not sufficient to ensure separation in phase space. This far reaching interconnection of plane wave components has interesting consequences for EPR-experiments too.

Recent experiments using beam chopper and time-of-flight analysis have also shown the persisting phase space coupling, even in cases where the overall beam does not show interferences at all\textsuperscript{36}). These experiments have underlined additionally the self-interference feature of neutron interference experiments as the mean occupation number of a single burst was in the order of 10\textsuperscript{-4} only.

**DISCUSSION**

All the results of the neutron interferometric experiments are well described by the formalism of quantum mechanics. According to the complementarity principle of the Copenhagen interpretation, the wave picture has to be used to describe the observed phenomena. The question how the well-defined particle properties of the neutron are transferred through the interferometer, is not a meaningful within this interpretation, but from the physical point of view it should be an allowed one. Therefore, other interpretations should also be included in the discussion of such experiments.
The particle picture can be preserved if pilot waves are postulated or if a quantum potential guides the particle to the predicted position. Related calculations have been performed for a simplified interferometer system [33]. Unfortunately, the results of these calculations are identical with the results of ordinary quantum mechanics and, therefore, to decide between both points of view remains an epistemological problem.

The newly discovered persisting phase space coupling in cases of large spatial shifts of the wave packets may bring some attendance to the action of plane wave components outside the packet.

We have always tried to perform unbiased experiments and do not wish to interfere with any epistemological interpretation of quantum mechanics. Perhaps in the future new proposals for experiments will be formulated, which permit a unique decision between different interpretations. As an experimentalist, one appreciates the pioneering work of the founders of quantum mechanics, who created this basic theory with so little experimental evidence. Now we have much more direct evidences, even on a macroscopic scale but, nevertheless, one notices that the interpretation of quantum mechanics goes beyond human intuition in certain cases. Only few aspects of the experiments discussed before should be mentioned again: How can every neutron have information about which beam to join behind the interferometer, when a slightly different energy exchange occurs in both beams inside the interferometer and the time constant of the beat effect is by many orders of magnitudes larger than the time of flight through the system? How can the interference pattern be influenced in a pulsed beam when the mean occupation number of a single pulse is in the order of $10^{-4}$ only? How can the wave packet influence each other when they are shifted more than their dimensions? These are the speakable and unspeakable questions of quantum mechanics.

Some recent experiments of our group which are related to fundamental physics problems have been discussed in this article. Several review articles can supplement a broader scope about the status of neutron interferometry [38] – 42).

ACKNOWLEDGEMENT

Most of the experimental results discussed in detail have been obtained by our Dortmund-Grenoble-Vienna interferometer group working at the high flux reactor in Grenoble, and some recent ones stem from our cooperation with the Columbia-Missouri group working at the MRRR-reactor. The cooperation within these groups and especially the cooperation with colleagues from our Institute, which are cited in the references, are gratefully acknowledged.

REFERENCES

6) U.Bonse, W.Hart: Appl.Phys.Lett. 6 (1965) 155
18) M.Namiki, S.Pascazio: Phys.Lett. 147 (1990) 430
40) H.Rauch: Contemp.Phys. 27 (1986) 345
EXPECTATIONS FOR NEUTRON EXPERIMENTS
-- An electron physicist's view --

Akira TONOMURA
Advanced Research Laboratory, Hitachi, Ltd.
&
Electron Wavefront Project, Research Development Corporation of Japan
Hatoyama, Saitama 350-03, Japan

ABSTRACT

An electron wavefunction's phase distribution can now be precisely measured to 1/100th of the electron wavelength using both electron holography and a "coherent" field-emission electron beam. This technique has opened up a new way to conduct thought experiments once regarded as experimentally impossible and also allows the ultra-fine measurement of material structures and field distributions.

INTRODUCTION

Neutron and electron beams can be used to directly demonstrate and test the predictions of quantum mechanics. In fact, they have enabled the detection of several kinds of phase shift due to quantum-mechanical phenomena. For example, neutron beams have been used to demonstrate the spinorial nature of fermions and the interaction of neutron waves with the earth's gravitation and rotation, and electron beams have been used to demonstrate the Aharonov-Bohm effect. There is no doubt that this field of massive particle interferometry will progress further with the development of brighter sources and high-precision interferometry techniques. In this paper, electron interference experiments are introduced in the anticipation that new and exciting neutron experiments will be performed.

Conventional electron microscopy uses the intensity of an electron beam to observe specimens. However, it has recently become easier to measure the relative phase of an electron wavefunction now that a two-beam electron interference pattern can be directly observed on a fluorescent screen as a result of the
development of the electron biprism\textsuperscript{1)} and a coherent field-emission electron beam\textsuperscript{2)}. Before these developments, interference patterns could only be recorded on film after a long exposure time in conventional electron microscopes. Furthermore, phases can now be measured with an accuracy of 1/100th of a wavelength using electron holography\textsuperscript{3,4)}. Due to this development, even thought experiments in fundamental physics have become experimentally feasible. In addition, the microscopic structure of materials at atomic scales and the microscopic distributions of electromagnetic fields can now be detected.

**ELECTRON INTERFERENCE**

--Demonstration of Wave-Particle Duality--

One of the predictions of quantum mechanics is that it is possible to perform a Young’s double-slit experiment with electrons even if only one particle passes through the apparatus at time. Feynman\textsuperscript{2)} referred to such an experiment as "impossible, absolutely impossible to explain in any classical way, and has in it the heart of quantum mechanics. This experiment has never been done in just this way, since the apparatus would have to be made on an impossibly small scale."

However, such an experiment has now become feasible\textsuperscript{6)} in a field-emission electron microscope equipped with an electron biprism\textsuperscript{1)} and a two-dimensional position-sensitive electron counting system\textsuperscript{7)} (see Fig. 1). Electrons emitted from a field-emission tip pass through the biprism, are detected by the electron counting system, and can then be displayed arriving one by one on a TV monitor. When there are few electrons, their distribution on the monitor seems quite random (see Fig. 2(a)). However, as the number increases, an interference pattern formed as if by two electron waves passing through both sides of the biprism becomes recognizable (Fig. 2(c), (d), and (e)). Even when the electron arrival rate is as low as 10 electrons/sec over the entire field of view, so that at most only a single electron exists at a time, the accumulation of single electrons still forms the interference pattern as shown in Fig. 2(e), as if the single electrons had passed through both sides of the biprism.

In quantum-mechanical terms, two partial electron waves overlap to interfere on the observation plane forming a probability interference pattern. When detected, the two overlapped partial electron waves can be observed as a single electron, never as two. It is interpreted that the measurement makes the extended wavefunction collapse into a single point instantly.
Fig. 1. Schematic diagram of single-electron interference experiment.

Fig. 2. Single-electron build up of the electron interference pattern: (a) \( N = 10 \), (b) \( N = 100 \), (c) \( N = 3000 \), (d) \( N = 20000 \), and (e) \( N = 70000 \).
AHARONOV-BOHM EFFECT

Another strange phenomenon in quantum mechanics is the Aharonov-Bohm (AB) effect\(^8\), which describes the fundamental interactions of electron waves with electromagnetic fields. The AB effect states that electrons can be physically influenced by a magnetic field without actually entering it. For example, if two electron waves travel in field-free regions on both sides of an infinite solenoid, the electron waves are physically influenced producing relative phase shift (see Fig. 3). Aharonov and Bohm attributed this effect to the vector potential surrounding the solenoid, in which the circulation integral does not vanish but is equal to the magnetic flux inside the solenoid. This effect is purely quantum-mechanical, since electrons pass through only field-free regions and therefore no force is exerted on them. Although the AB effect is a straightforward consequence of the Schrödinger equation, it was the center of a long controversy until recently, since it is so contradictory to conventional wisdom that various assertions have been made concerning its physical implications and even its existence.

The significance of this effect increased in the late 1970's\(^9\), when the theory of gauge fields was revived as the most probable candidate for the unified theory of all fundamental interactions in nature. In this theory, vector potentials are extended to gauge fields and regarded as fundamental physical quantities. The AB effect demonstrates the physical reality of gauge fields.

![Diagram of Aharonov-Bohm effect](image)

Fig. 3. Aharonov-Bohm effect.
Of a series of experiments we made, the last is considered to be the most conclusive, and is introduced here. Instead of a straight solenoid, a toroidal ferromagnet was used. An infinite solenoid is experimentally unattainable, but an ideal geometry can be achieved by a finite toroidal magnet\(^{10}\). Furthermore, the toroidal magnet was covered with a superconducting niobium layer to completely confine the magnetic field.

A sample with such a complicated structure should be smaller than the transverse coherence length of an electron beam, 10 \(\mu\)m, say, and thus should be fabricated with the most advanced photolithography techniques. The resultant sample is shown in Fig. 4.

The relative phase shift was measured between two electron waves passing through the inside of the hole and outside the toroid at 5 K\(^{11}\). Measurements were made for many samples with different magnetic flux values. However, only two phase shifts, 0 or \(\pi\), were observed, as shown in Fig. 5. The conclusion is obvious -- a relative phase shift of \(\pi\) is produced even when the magnetic field is confined within the superconductor and is shielded from the electron beam. This proves that the AB effect exists.

But why is the phase shift either 0 or \(\pi\)? This quantization of the phase shift provides key evidence for the complete shielding of the magnetic field by the covering superconductor: When a magnetic flux is completely surrounded by a superconductor, the magnetic flux is quantized in \(h/2e\) units. Since a magnetic flux of \(h/2e\) produces a phase shift of \(\pi\), the relative phase shift is 0 or \(\pi\) depending on whether the number of trapped flux quanta is even or odd.

---

Fig. 4. Toroidal magnet covered with superconductor:
(a) Scanning electron micrograph, and (b) Schematic diagram.
MAGNETIC FIELD OBSERVATION

The AB effect tells us that a phase shift of $2\pi$ is produced between two electron beams enclosing a magnetic flux of $\hbar/e$. It can therefore be concluded that an electron interference micrograph displays the flow of magnetic flux directly and quantitatively\cite{12}. Contour fringes in the micrograph indicate magnetic lines of force, and a magnetic flux of $\hbar/e$ flows between each pair of adjacent contour fringes. It has actually become possible to make such electron interference micrographs using an electron holography process\cite{4}, which consists of forming an electron hologram with a coherent field-emission electron beam and reconstructing an optical image with a laser beam.

An example of an interference micrograph is shown in Fig. 6. The specimen is a fine particle of cobalt. When observed with an electron microscope which displays the intensity of the transmitted electron beam, only the triangular outline can be observed. However, in this interference micrograph, two kinds of fringes appear. Those parallel to the three edges indicate that the thickness increases linearly to 550 Å from the edges, and those in the inner region where the thickness is uniform indicate magnetic lines of force. The smoothly rotating magnetization becomes observable at a glance even in such a fine particle.

Fig. 5. Electron interferograms indicating relative phase shift:
(a) Phase shift = 0, and (b) Phase shift = $\pi$. 
Since the flux itself is observed, its dynamic behavior can be observed\textsuperscript{13}). In this case, after electron holograms were dynamically recorded on videotape, an interference micrograph of each frame was numerically reconstructed, and again recorded on videotape. Although off-line, flux dynamics could be observed with a time resolution of 1/30 of a second.

![Schematic diagram](image)

**Fig. 6.** Interference micrograph of Co fine particle.

![Figures](image)

**Fig. 7.** Dynamic observation of trapped flux lines near $T_c$: (a) 0 seconds, (b) 0.13 seconds later, and (c) 1.33 seconds later.
The experiment was carried out as follows. Trapped fluxes in a superconducting Pb thin film remained stationary at 5 K. However, when the sample temperature was raised, the flux diameter gradually increased. Just below the critical temperature, the flux began to move. Fig. 7 shows a section from the videotape which recorded this movement.

Three fluxons in the upward direction are trapped in the superconductor and their magnetic lines of force can be seen in Fig. 7 (a). At 0.13 seconds, the fluxons moved suddenly to the left after only the lapse of a single frame. Two upward fluxons and two downward fluxons are connected by magnetic lines. At 1.33 seconds, downward fluxons moved to the right and only a broad single magnetic line remained.

CONCLUSIONS

The advent of a coherent electron beam has opened up a new way to visualize the phase distribution of the electron wavefunction. This technique has enabled thought experiments in fundamental physics to be actually carried out, and provides a new way of observing microscopic objects and fields.

REFERENCES

1) G. Möllenstedt & H. Düker, Naturwissenschaften 42 (1955) 41.
2) A. Tonomura et al., J. Electron Microsc. 28 (1979) 1.
FUNDAMENTAL PHYSICS WITH ULTRACOLD NEUTRONS

Masahiko UTSURO

Research Reactor Institute, Kyoto University
Kumatori-cho, Sennan-gun, Osaka, 598-04 Japan

ABSTRACT

A novel property of the neutron with the energy below about 0.2 μeV so called ultracold neutrons showing the total reflection even under normal incidence and the application of the possibility of the neutron storage in a closed vessel are reviewed. The UCN container vessel named a neutron bottle has the advantages of the long observation time for neutrons as well as the possibility of a larger number of decay events of the neutrons in the bottle comparing to beam type experiments for thermal and cold neutrons. These advantages can be applied for the studies on phenomena related to the fundamental physics and elementary particle physics. Another application of the UCN properties appears in the use of various mirrors for the studies in wave mechanics and neutron optics. The recent progress in UCN facilities and experimental devices are also described briefly.

INTRODUCTION

A theoretical possibility of neutron storage in a closed vessel was in the first time pointed out in 1959 by Zel'dovich\(^1\) with quantitative estimations based on the known property of total reflection of very slow neutrons below the critical velocity of about 5 m/s. He also predicted the advantage of long observation time of the stored neutrons and the use of liquid helium to cool the neutrons in the cavity. In a following paper by Vladimirskii\(^2\) with the analyses of conditions for the use of magnetic channels and bottles for cold neutrons, such neutrons to be confined in a vacuum region were named ultracold neutrons (UCN). Further, in an instructive textbook on low energy neutron physics by Gurevich and Tarasov\(^3\), a whole chapter was devoted to UCN. The first experimental observations of UCN were reported by Luschikov \textit{et al.}\(^4\) at Dubna with a horizontal guide tube in a 6kW reactor provided by shutter-detector sets at the exit end, and independently by Steyer\(^5\) at Munich with a vertical guide and time-of-flight method in a 4MW reactor. The gravity effects on UCN was clearly observed and agreed with the expectation, and furthermore the UCN storage in a closed guide tube was demonstrated\(^5\). Although the experimental principles of these inventions on UCN were rather simple, the most of the difficulties came from the extremely low intensities of the UCN as Zel'dovich first indicated with the fraction of the order of $10^{-9}$ of UCN in a room temperature Maxwellian distribution.

Owing to the recent developments in the fields of reactor cold sources, very cold neutron facilities, neutron optics and optical devices, during some quarter of a century from the first observations of UCN, the available UCN intensities were significantly increased, as in the typical facility with a turbine UCN generator at ILL, Grenoble illustrated later. The present paper will describe, with showing some of these developments in UCN technologies, peculiar interests and some future possibilities in the field of fundamental physics with UCN.
CHARACTERISTICS OF ULTRACOLD NEUTRONS

The usual thermal neutrons with the energy of room temperature are well known to penetrate deeply into various materials and scattered by individual nuclei. However, UCN with the energy below about 1/10,000 of thermal neutrons show many peculiar phenomena due to the wave properties of the neutrons. These characteristics of UCN are illustrated in Fig.1, where following to the introduction of Alice-in-Wonderland in a universal mirror by Adair\(^2\), we are going to play with Alice, here not in Wonderland, but in the world of physics. Alice drops the ball of a neutron from the height of 3.0m on nickel floor, then the ball sinks into the floor, while from the height of 1.8m, then it bounds totally reflected, and the wavelength would vary from about 50\(\mu\)m to the order of \(\mu\)m at the uppermost position.

In the case of thermal neutrons, Bragg scattering occurs in ordered coherent scatterers as the typical phenomena of wave properties. In the lower energy region, i.e. in the much longer wavelength region of UCN, the neutron wavelength extends over a number of atoms in the condensed matter. Such a situation as the multiple scattering of waves by a random distribution of scatterers was first considered by Foldy in a general formalism in detail\(^3\) about 10 years after the discovery of the neutron, where the index of refraction \(n\) can be given with the scattering amplitude of the scatterer according to the relation,

\[
a = \frac{k'}{k} = \sqrt{1 - 4\pi N\mathcal{F}/k^2},
\]

where \(k'\) and \(k\) are the propagation constants in the medium and in vacuum, respectively, \(N\) the density of scatterers and \(\mathcal{F}\) is the scattering amplitude.

This equation predicts the situation occurs such as no propagating waves exist when

\[
k^2 \leq 4\pi N\mathcal{F}, \quad \mathcal{F} < 0.
\]

The behavior of UCN in most kinds of materials is just the typical case of the situation that UCN could not propagate into the materials from vacuum but totally reflected back to the vacuum, and further analogous situations can occur also at the interface from weak scatterer medium to strong scatterer one. Actually, a neutron feels positive potential of \(\theta = 2\pi A^2/\hbar\), entering from vacuum to most of materials as shown in Table 1, with the critical velocity \(v_c\) of several m/s for the total reflection of the neutron. In Table 1, two kinds of values are listed for magnetic materials, because of the magnetic dipole

---

\begin{center}
Table 1. Scattering potential for various materials
\end{center}

\begin{tabular}{|c|c|c|}
\hline
Substance & \(\theta\) (\(\mu\)eV) & \(v_c\) (m/s) \\
\hline
Al & 0.0541 & 3.22 \\
Cu & 0.185 & 5.6 \\
Graphite & 0.155 & 5.4 \\
Be & 0.25 & 6.9 \\
D\(_2\)O & 0.166 & 5.6 \\
Fe & 0.350 & 8.2 \\
Ni & 0.090 & 4.15 \\
Ti & 0.27 & 7.2 \\
H\(_2\)O & 0.20 & 6.2 \\
Ti & 0.050 & --- \\
H\(_2\)O & 0.0146 & --- \\
\hline
\end{tabular}
moment of a neutron, in which upper values correspond to the neutron spin parallel to the magnetic field, lower ones to the anti-parallel. The wavelength of the neutron can be derived by the equation \( \lambda = 396/\nu \) (nm), with \( \nu \) in units of m/s.

The loss probability of UCN per bounce was studied by Groshev(10) by storing UCN in bottles made of various material mirrors, and the results showed larger loss probabilities than that of an elementary theory for a clean flat surface, as shown in Fig. 2, and the possible reasons are now thought to be the surface incompleteness mainly due to hydrogenous contamination on the mirror with the thickness of several nm. Actually, the use of non-hydrogenous liquid mirror gave much smaller loss probability of \((2.3) \times 10^{-5}\) for the bottled neutrons(13).

A special type of neutron mirror named "supermirror" made of multilayers is developed(12) as shown in Fig. 3 with a larger critical velocity of reflection than single layer mirrors. If high quality supermirrors with desired sizes become available, then the number of stored neutrons in the bottles will considerably be increased because of the neutron density proportional to \( r^2 \) in a Maxwellian distribution.

---

Fig. 2 Absorption coefficient for UCN in a copper trap plotted versus the neutron velocity. 1 elementary theory; 2 elementary theory but with 2.6 times enhanced \( \mu \)-value; 3 model of a soft potential step for the wall with the smooth edge 11nm; 4 hydrogenous contamination on the wall with a thickness 5.5nm.

---

Fig. 3 Schematic drawing of a supermirror structure with the reflection mechanism and the measured reflectivity of a Ni-Ti supermirror developed at KUR.
A. Long Time Observations of Bottled Neutrons

In order to detect a much smaller energy change of a particle, we must expend much longer observation time for the particle in the experiment, according to the principle of uncertainty. The experimental efforts now being continued to detect the smallest energy difference never attained yet would be the search for the electric dipole moment of a neutron. We will play again with Alice in Fig. 4, where Alice is looking at the surface pattern of the spinning ball of a polarized neutron. If Alice could distinguish the dipole colored pattern, i.e., the electric dipole moment of a neutron, she would recognize the dipole is parallel or anti-parallel to the direction of the spinning of the ball. Either one is the situation in the real world where the clock turns in the correct direction, while the other should be the situation in the Wonderland in a Mirror where the clock turns in reverse direction. Thus, if she could detect the dipole electric pattern on the neutron, she can tell us the time-reversal invariance is violated in the neutron. However, since the possible electric dipole moment (EDM) of the neutron should be extraordinary faint, she must spend much longer observation time before saying anything, due to the uncertainty principle. The bottled UCN would be able to improve much more the length of the observation time to thousands seconds comparing to milliseconds in the conventional neutron beam experiments, for the detection of possible very small change in the resonance frequency in magnetic and electric fields in the EDM chamber. A practical structure of the experimental device will be shown in the next chapter.

Another application of UCN bottle is of course the precise measurement of the free neutron lifetime which is related to such important problems as the axial vector coupling constant in the weak interaction, helium abundance in the early universe and also the solar neutrino problem. The most accurate value at present for the neutron lifetime was reported from the liquid walled bottle experiment(3).

B. Decay Experiments of Bottled Neutrons

We would like to be concerned another trial of Alice-in-Wonderland going to distinguish where she is, in the real world or in the Mirror with the clock reversing. Now, she is looking at the event of the decay of a polarized neutron. She would be interested in the direction of the particles emitted in the neutron decays, and if she could specify the
two directions among three, i.e. the proton, the electron and the anti-neutrino, then drawing the correlation diagram between the directions of the spin and the emissions would decide the three vectors always lying on a common plane, or such events as shown in Fig. 5 are included. In the latter case, she would come to know where she is, in the real or in the Mirror, and could tell us there is a possibility of the time-reversal invariance violated.

Up to now, the experiments of three vector correlations in the $\beta$-decay of polarized neutrons were carried out with a collimated beam in a narrow chamber, and no effective asymmetries to the decay-plane were derived\textsuperscript{142}. If we consider to employ a large volume UCN bottle, we can expect a larger number of $\beta$-detections than that in the beam experiments would be possible as estimated in the next chapter.

Another applications of the attractive properties of UCN bottle were discussed in the case of neutron-antineutron oscillations, one is the idea introduced by Yoshiki\textsuperscript{153} to undertake a possible accumulation of antineutron amplitudes on the successive wall-reflections in the bottle with a specified technique, and the other study\textsuperscript{163} is the estimation of the advantage of much longer flight times of UCN in the oscillation experiment in a bottle, comparing to neutron beam chambers. Such experiments might become a practical scope with a more intense supply of UCN in future.

C. Wave Mechanics with UCN

Long wavelength and very slow velocity of UCN could bring possibilities of various kinds of experiments for quantum mechanical studies of neutron waves, some of them are the studies of the behavior of massive neutron waves in optical structures\textsuperscript{17}\textsuperscript{18}, and in another program would be a macroscopic control of neutron waves in very long wavelength region with multilayer devices\textsuperscript{19}.

RECENT DEVELOPMENTS IN UCN FACILITIES AND EXPERIMENTS

A. Vertical Facility at ILL

The most intense supply of UCN up to now was realized in the vertical combination shown in Fig. 6 of a liquid deuterium cold source directly connected with a guide tube for very cold neutrons (UCN) with the velocity of about 50m/s and a mechanical velocity shifter.
from VCN to UCN, named neutron turbine developed by Steyer\textsuperscript{203} in Munich. The cold source is located in the reflector region of a high flux reactor of 57MW, where the thermal neutron flux is about $4.5 \times 10^{14}$ n/cm²s, the VCN gain factor of the cold source is about 40. The turbine consists of a rotating wheel provided by a number of semicircular mirror blades of nickel with the moving velocity of about 25m/s, i.e., about half the velocity of incident VCN to generate UCN according to the working principle of the axial turbine. The UCN output intensity of the ILL turbine\textsuperscript{21} is about $2.6 \times 10^4$ UCN/cm²s with 5 UCN exit ports for various kinds of UCN experiments such as the neutron lifetime, the neutron EDM, the gravity diffractometer, the neutron microscope, and so on. The lifetime experiments with a liquid walled bottle at ILL gave already most precise result of $887.6 \pm 3\text{ns}$\textsuperscript{13}. Further, in Fig.7 the schematic structure of a practical EDM apparatus with bottled UCN at ILL is shown\textsuperscript{22}, where the storage time of about 80s is measured with the resonance method developed by N. Ramsey. The present sensitivity of the experiments reported overcoming the level of $10^{-26}$ e.cm, the existence of a finite amount of the moment is not yet concluded. The possible improvements of the experimental accuracy are thought to reduce systematic errors and to increase the storage volume.

B. Horizontal Facility at KUR

A liquid deuterium cold source\textsuperscript{23} is installed as shown in Fig.8 in the graphite thermal column of 5MW KUR, providing VCN with the velocity of 50–150m/s to the horizontal VCN guide tube\textsuperscript{24} connected with a supermirror tube\textsuperscript{25} via a VCN bender with the characteristic velocity of 82m/s for adjusting the VCN feed direction to the turbine port\textsuperscript{26}. The measured VCN gain factor of the horizontal cold source showed the minimum value of about 40 at the VCN velocity of about 150m/s and gradually decreasing to about 15 at 40m/s. The blades of the turbine consist of 32 sets of three flat supermirrors and rotates with the velocity of about 25m/s as the original design providing the measured UCN gain factor of about 20 with the cold source operation. With the UCN output of the supermirror turbine, some UCN transmission experiments and developments of the UCN bottle for neutron decay studies are now in progress.

For the decay experiment, it was shown from numerical studies by Yamaguchi\textsuperscript{27} that a continuous feed of UCN to the bottle with a large volume made of supermirrors with higher critical velocity than ordinary metal mirrors is much advantageous. If we consider to employ a large volume UCN bottle, for example with a size of 65cm in diameter and 150cm in
length, charged with a continuous UCN filling through a 100cm$^2$ port with the flux of 100 UCN/cm$^2$·s, in place of the narrow chamber as reported$^{141}$, we can expect from the numerical studies that a larger number of $\beta$-detections of the order of $10^7$·8 per year would be feasible. The calculation showed also that the situation benefits further by the use of high quality supermirrors for the bottle wall. These numbers indicate the improvements of experimental sensitivities in orders to that in the beam experiments will be possible for decay $\beta$-spectrum and decay particles asymmetries measurements with the bottled UCN densities of the recent supply facilities. As for one of the preparations for these decay experiments in bottles, large area semiconductor $\beta$-detectors with UCN mirror surface having a satisfactory linearity and energy resolution of about 35keV were developed by Miyachi at INS, University of Tokyo. Furthermore, considering the higher gain factors measured for a little faster VCN than about 50m/s as mentioned above, the UCN output of the present turbine would be improved with a factor of 2·3 at a little higher rotation speed.

C. Superthermal Helium Converter at JRR-3

Another principle to produce UCN by using a superfluid helium converter applies the energy-momentum relation of the quantum liquid Hel showed in Fig.9, which indicates at the intersection point with the energy of about 12K with the curve for a neutron, almost whole of the energy of the cold neutron should be transferred to the liquid and converted to UCN. This idea was proposed and studied in detail by Golub$^{28,29}$, and now developed by Yoshiki$^{30}$ for the purpose of the EDM experiment with the bottled UCN. In Fig.10 the arrangement of the cryostat at JRR-3 for the studies of Hel properties in UCN production is shown. From the measurements using the velocity-analysed incident neutrons the value for the wavelength of the UCN production process was decided as 0.878±0.006 mm, and the temperature variation of the UCN storage lifetime in the Hel bottle was also studied.
CONCLUDING REMARKS

Several aspects of the growing interests in the fundamental physics research with ultracold neutrons were introduced within a very limited space of the present article. There are many tasks to be studied for the full understandings of the experimental results for example about the possible significant loss factors in the UCN extractions, UCN storage times in material bottles, methods of efficient polarizations of UCN in the bottle, and so on. Further developments for intense production of UCN and for the experimental utilizations of UCN with a high reliability would be of course fundamental requirements. Applications of recent results in neutron optics and optical devices would also bring significant improvements and new proposals in the UCN studies, such as the use of high quality supermirrors and magnetic multilayers, and in the last, not in the least, studies on UCN detecting system would also be necessary works for the progress of the present field. With the cooperations of these efforts, the UCN for the fundamental research will become more interesting area among the neutrons as microscopic probes.

REFERENCES
2) V.V. Vladimirkii:ibid. 39, 1062(1960).
10) L.V. Groshev et al.:JINR Communication R3-9534(Dubna 1976).
15) H. Yoshiuki:KEK Reprint 80-10, Tsukuba, Japan(1980);Proc. ICANS-IV, KEK.
NEUTRON RADIOMETRY - STATUS AND INTERNATIONAL PROSPECTS

John P. BARTON

NRE INC.
1422 Vue Du Bay Court, San Diego, CA 92109, USA

ABSTRACT

Neutron radiography (or radiology) is a diverse field that uses neutrons of various energies, subthermal, thermal, epithermal or fast, in either steady state or pulsed mode to examine objects for industrial, medical, or other purposes, both microscopic and macroscopic. The applications include engineering design, biological studies, nondestructive inspection and materials evaluation. In the past decade, over 100 different centers in some 30 countries have published reports of pioneering activities using reactors, accelerators and isotopic neutron sources. While film transparency and electronic video are most common imaging methods for static or in motion objects, respectively, there are other important data gathering techniques, including track etch, digital gauging and computed tomography. A survey of the world-wide progress shows the field to be gaining steadily in its diversity, its sophistication and its importance.

INTRODUCTION

It is an honor to present this invited paper reviewing neutron radiography within this international conference entitled Neutrons as Microscopic Probes. Most of the papers in the conference discuss scattering techniques to study microscopic details of crystal structure. Neutron radiography shares a common interest in neutron sources and neutron physics, but it uses the microscopically small neutron primarily to obtain macroscopic information. The optically enlarged image showing individual boron fibers in a metal composite provides an example of the small scale neutron radiography capability. A neutron radiograph of a full size motorcycle has been used to illustrate the larger scale possibilities.

Neutron radiography depends on the ability of neutron radiation to penetrate certain materials (typically dense metals) more readily than enclosed elements of interest (typically those containing hydrogen). The techniques can sometimes provide important information that cannot be obtained by conventional X-radiography or alternative inspection methods. In most cases the spectrum of predominantly thermal neutrons emergent from a moderated neutron source will provide the contrast needed. Of course, by selection of different neutron energies, the capabilities can be changed significantly.

SOURCES

The neutron beam is usually extracted through the source shielding using a divergent collimator design. The neutron flux incident on the object is the flux at the
collimator input reduced by the square of the collimator ratio of length L to input diameter D.

Neutron sources ranging from very high flux to relatively low flux each have a role to play in neutron radiography. At the end of this conference we shall visit the high flux reactor JRR-3 which has three operational neutron radiography systems, one for nuclear fuel studies, another for non radioactive material studies, and a cold neutron capability. The reactors JRR-2 (10 MW), JRR-4 (3.5 MW) and NSRR (pulsed reactor) at JAERI have also been applied to neutron radiography. Saclay and Petten are other centers that have high flux reactors with facilities designed for fuel, thermal and cold neutron radiography. Sandia National Laboratory in the USA has an annular core pulsed reactor neutron radiography capability comparable with NSRR (Table 1). Low cost reactors such as the 10 KW L88 solution type in the USA, the MIRENE reactor in France, and the 1 W reactor at Kinki University in Japan can also be useful for certain applications. The one watt reactor provides a neutron flux of $3 \times 10^5$/$cm^2 \cdot s$ at L/D 22. In Taiwan the so called zero power reactor has been recently upgraded to 30 KW specifically to meet various industrial neutron radiography demands.

**TABLE 1**

**Comparable NR Systems - Approximate Figures**

<table>
<thead>
<tr>
<th>NR TYPE</th>
<th>CENTER</th>
<th>REACTOR</th>
<th>L:D</th>
<th>n/$cm^2 \cdot s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>JAERI</td>
<td>JRR-3</td>
<td>170</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>PETTEN</td>
<td>HFR</td>
<td>400</td>
<td>$2 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>SACLAY</td>
<td>OSIRIS</td>
<td>150</td>
<td>$6 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>SANDIA</td>
<td>ACPR</td>
<td>110</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td>Cold</td>
<td>JAERI</td>
<td>JRR-3 GUIDE</td>
<td>150</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td></td>
<td>PETTEN</td>
<td>HFR-FILTER</td>
<td>150</td>
<td>$2 \times 10^5$</td>
</tr>
<tr>
<td></td>
<td>SACLAY</td>
<td>ORPHEE-GUIDE</td>
<td>150</td>
<td>$2 \times 10^8$</td>
</tr>
</tbody>
</table>

Accelerators in use for neutron radiography include cyclotrons, van de graaff machines, and sealed tube neutron generators. In Japan, of twenty operating neutron radiography systems nine use accelerators. High yield D-T accelerators and special radio frequency quadrupole accelerators are being developed for neutron radiography applications in Europe and the USA.

Also isotopic neutron sources, principally Californium-252, are being applied.
The neutron beam flux of the 50 mg Cf-252 source in use for aircraft inspection is similar to that detailed above for the 1 Watt reactor.

**IMAGING**

Four major categories of neutron imaging technology have been developed so far. The direct exposure technique uses a neutron converter, such as vapor deposited gadolinium, held by a vacuum cassette against fine grain single emulsion radiographic film. A typical exposure requires $10^5$h/cm² and provides a resolution comparable in quantity to the finest grain industrial or medical X-ray film. Image quality standards have been developed so that film neutron radiography can provide approved quality control for inspections critical to the safety of systems such as aircraft, space rockets or nuclear reactors.

The second category of neutron detection is the activation transfer method, where dysprosium or indium converter sheets enable a highly radioactive object to be neutron radiographed without gamma radiation reaching and fogging the film. The third category is track etch imaging where a neutron converter, typically boron, is exposed to the neutron beam together with a cellulose nitrate sheet. The sheet is later chemically etched. This method is also insensitive to gamma ray interference, and is of particular value where high precision dimensions are needed for nuclear fuel swelling measurements. The fourth neutron imaging category is dynamic imaging where a scintillator and video chain are used to provide images on a television monitor. Such electronic imaging lends itself to computer processing and color enhancement. Both film and electronic imaging techniques have been extended to provide neutron computed tomography for special applications.

**HISTORICAL CYCLES**

It was at a neutron scattering conference similar to this, but in London in 1961, that the idea of neutron radiography first occurred to this author. Dr. Bacon, author of an early book on neutron diffraction, described how crystal monochromators were lined up with reactor beams by noting the shadow on a film. Could such neutron beams and imaging open for medical applications a whole new field similar to X-radiography? After some months of experimenting, alone in Europe at that time, it was discovered that Kallman in Berlin and Thewlis in Harwell had previously written on the subject. Independently McGonnagle, Watts, and Berger were starting work in Chicago. Since that start to over 30 years of continuous effort there has been little overlap between the conference schools of neutron scattering and neutron radiography. It is appropriate then to return full cycle in reporting back to you. Neutron radiography and neutron scattering share many common interests in addition to shared utilization of neutron sources.

The history of neutron radiography development is recorded in its publications. In the first 30 years, 1932-1962 there were relatively few publications (just five or so), but between 1963 and 1993 the activity expanded significantly as summarized in a direct mail neutron radiography newsletter², and in a series of topical conferences.⁴ Table 2 shows the distribution of the eighty research institutes and industries in twenty
TABLE 2

Centers Reporting at the Fourth World Conference on Neutron Radiography, May 1992

<table>
<thead>
<tr>
<th>USA</th>
<th>JAPAN</th>
<th>W. EUROPE</th>
<th>OTHER</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Institute</strong></td>
<td><strong>Institute</strong></td>
<td><strong>Institute</strong></td>
<td><strong>Institute</strong></td>
</tr>
<tr>
<td><em>Argonne National Laboratory</em></td>
<td><em>Fujita-Gakuen Health University</em></td>
<td><em>Austria</em></td>
<td><em>Australia</em></td>
</tr>
<tr>
<td><em>Cornell University</em></td>
<td><em>Japan Atomic Energy Research Institute</em></td>
<td><em>Atom Institute of the Austrian Universities</em></td>
<td><em>Nuclear Science and Technology Organisation</em></td>
</tr>
<tr>
<td><em>Massachusetts Institute of Technology</em></td>
<td><em>Kanazawa Dental College</em></td>
<td><em>Denmark</em></td>
<td><em>Brazil</em></td>
</tr>
<tr>
<td><em>The Pennsylvania State University</em></td>
<td><em>Himeji-Dokkyo University</em></td>
<td><em>Riso National Laboratory</em></td>
<td><em>Instituto de Pesquisas Energéticas e Nucleares</em></td>
</tr>
<tr>
<td><em>Sandia National Laboratory</em></td>
<td><em>Kobe University</em></td>
<td><em>France</em></td>
<td><em>Canada</em></td>
</tr>
<tr>
<td><em>Texas A&amp;M University</em></td>
<td><em>Kyoto University</em></td>
<td><em>CEA Saclay</em></td>
<td><em>Atomic Energy of Canada</em></td>
</tr>
<tr>
<td><em>University of California at Santa Barbara</em></td>
<td><em>Murayama Institute of Technology</em></td>
<td><em>CEN Grenoble</em></td>
<td><em>McMaster University</em></td>
</tr>
<tr>
<td><em>University of Chicago</em></td>
<td><em>Nagoya University</em></td>
<td><em>Centre Henri Becquerel</em></td>
<td><em>Royal Military College of Canada</em></td>
</tr>
<tr>
<td><em>University of Michigan</em></td>
<td><em>Rikkyo University</em></td>
<td><em>Sodertem</em></td>
<td><em>Chile</em></td>
</tr>
<tr>
<td><em>University of Virginia</em></td>
<td><em>University of Tokyo</em></td>
<td><em>Schlumberger Industries</em></td>
<td><em>Chilean Air Force</em></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Industries</th>
<th>Industries</th>
<th>Industries</th>
<th>Industries</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>AccSys Technology, Inc</em></td>
<td><em>ASK Co., Ltd</em></td>
<td><em>Bologna University</em></td>
<td><em>Central Research Institute for Physics</em></td>
</tr>
<tr>
<td><em>Aerosec Operations, Inc</em></td>
<td><em>Japan Fine Ceramics Center</em></td>
<td><em>ENFRICERCH</em></td>
<td><em>Institute of Nuclear Physics</em></td>
</tr>
<tr>
<td><em>Bettis Atomic Power Laboratory</em></td>
<td><em>Japan Steel Works, Ltd</em></td>
<td><em>ENEAA/INN</em></td>
<td><em>Physics of the Hungarian Academy of Sciences</em></td>
</tr>
<tr>
<td><em>C.W. Peters, Nuclear Diagnostics Systems</em></td>
<td><em>Mitsubishi Atomic Power Industries, Inc</em></td>
<td><em>The Netherlands</em></td>
<td><em>India</em></td>
</tr>
<tr>
<td><em>General Atomics</em></td>
<td><em>Shin-Etsu Chemical Co., Ltd</em></td>
<td><em>European Space Agency</em></td>
<td><em>Bhabha Atomic Research Centre, India</em></td>
</tr>
<tr>
<td><em>Industrial Quality, Inc</em></td>
<td><em>Sumitomo Heavy Industries, Ltd</em></td>
<td><em>Joint Research Centre of the Commission of the European Communities</em></td>
<td><em>Ben Gurion University of the Negev</em></td>
</tr>
<tr>
<td><em>Lockheed - ESC</em></td>
<td><em>T. H. Poh, Tawo Co., Ltd</em></td>
<td><em>Netherlands Energy Research Foundation</em></td>
<td><em>Soreq Nuclear Research Centre</em></td>
</tr>
<tr>
<td><em>LTV Aerospace &amp; Defense</em></td>
<td><em>T. Sogabe, Toyo Tanso Co., Ltd</em></td>
<td><em>Switzerland</em></td>
<td><em>Russia</em> (I.V. Kurchatov Institute of Atomic Energy, <em>Slovakia</em> (J. Stefan Institute)</td>
</tr>
<tr>
<td><em>Mason &amp; Hanger Pantex Plant</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>McClellan AFB</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>NASA Johnson Space Center</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>NRE, Inc</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>P.J. Cooper, Science &amp; Engineering Associates, Inc</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Physitrion, Inc</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Science Applications International Corporation</em></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*If 1992*
three countries reporting in the Fourth World Conference on Neutron Radiography currently in the publication process.

ENERGY APPLICATIONS

The value of neutron radiography research and development is realized when it leads to application for important problems. In this review we will start with the contribution of neutron radiography to the field of nuclear energy. Neutron radiography of highly radioactive nuclear fuel specimens can be performed using massive shipping casks with external reactor beams or, more conveniently, underwater systems such as at the Saclay Osiris reactor, where fuel specimens can be easily moved from the core irradiation position to inspection and back. The importance of neutron radiography for studies of nuclear fuel before or after irradiation has been such that several nuclear reactors have been built especially for fuel neutron radiography. Examples are at Cadarache in France, and at the Argonne Hot Cell complex in the USA.

Some examples on neutron radiography applications to nuclear fuel studies include identification of clad failure by water ingress, measurement of external fuel pellet dimensional changes, and examination of fuel internal changes using epithermal neutrons. Accident behavior studies such as loss of coolant simulations are also evaluated using neutron radiography.

The plans in Japan concerning fast breeder power reactors, highlighted recently by a major shipment of plutonium from France, invites mention of the ability of neutrons for studies of plutonium fuel. The freshly manufactured mixed oxide fuel for the Fast Flux Test Facility at Hanford was inspected one hundred percent by a specially installed Triga reactor using a large area vertical collimator. This can provide checks against misplaced blanket pellets, unacceptable pellet voids, and unacceptable size of plutonium oxide agglomerations. Studies of plutonium fuel behavior in accident conditions provide results that can be even more dramatic.

Technologies applicable to fast breeder reactor development include computed tomography of fuel bundles, and use of the fast neutron hodoscope at the Argonne Treat reactor to image the fission neutron pattern emerging from a fuel assembly in test conditions. Neutron radiography evaluation of raw zirconium required for manufacture of fuel rod cladding has been undertaken on a massive scale. By use of subthermal neutrons the crystalline zirconium is rendered relatively transparent and small impurities such as hafnium can be detected. A special cold neutron source system using liquid methane was installed on a Mark F Triga reactor at the General Atomics Company for this application.

TRANSPORT APPLICATIONS

The safety of each jet aircraft flight depends on thousands of turbine blades making millions of revolutions without failure. To eliminate the risk of a turbine blade coolant channel being blocked at manufacture, every blade is inspected using neutron radiography. Neutron radiography of these expensive but important turbine blades is a major international business involving nuclear reactors in Asia, Europe, and North
America. In addition to routine inspection for blockage of coolant channels, special interests could include hydride embrittlement of the titanium-aluminum alloy in jet engine fan blades. Neutron computed tomography has been indicated as a tool in crashed aircraft investigations involving failed jet engines.

Because critical control panels of modern aircraft are constructed of paper thin aluminum, and because this aluminum can corrode if moist, maintenance inspections for hydrogen aluminum corrosion can be important to ensure air worthiness over airframe lifetimes that may exceed 20 years. The aluminum corrosion product contains hydrogen that can be revealed by neutron radiography. An Air Force maintenance center in the USA has recently constructed two neutron radiography systems, one using a maneuverable californium-252 neutron source together with robotics to obtain scans of intact aircraft, and the other a higher flux Triga reactor neutron source for higher sensitivity inspection of detached parts. Hidden moisture and honeycomb corrosion that cannot be detected by X-rays is clearly seen using this neutron radiography. One of the first types of aircraft inspected has been the F-15, an aircraft that is also of interest to the Mitsubishi aircraft maintenance division in Nagoya, Japan. The question of applicability of neutron radiography to commercial aircraft maintenance is a subject for future study.

**FOOD AND SHELTER APPLICATIONS**

Research that improves food production may rank in importance along with energy and transport in view of the increasing world population. Neutron radiography can provide agronomists and soil scientists with a unique method for sequential studies of undisturbed seed germination, plant root growth, and moisture uptake in controlled conditions such as simulation of frosts and droughts. Valuable work in this area has been performed recently at the University of Tokyo in collaboration with Rikkyo University, in addition to work in several other countries.

Neutron radiographic methods are also being developed to improve building methods with porous materials such as concrete and brick. Water permeability of importance to dams, bridges and other building foundations has been studied this way in both Austria and China. Neutron radiography has been developed in Germany to study cement and plastic behavior inside concrete. Methods to evaluate concrete microcracking have been used in the USA. In Czechoslovakia neutron radiographic methods are officially standardized for testing water protective agents in building materials.

**HEALTH AND CONSUMER PRODUCT APPLICATIONS**

Several centers have reported the use of neutron radiographic techniques for research in medicine and biology. One application, for example, involved an operation on a person to remove sections of jaw bone containing hidden cancer. Another study in Japan provided information on the causes of gallstone formation. Neutron radiography is also being developed as a tool in dentistry research. Neutrons can, for example, penetrate metal crowns to reveal internal dental defects. Also, because neutrons penetrate relatively dense tooth material and reveal internal soft tissue, neutron radiography can help develop root canal and other endodontics technology.
Examples of general consumer product industry applications for neutron radiography include studies of solders, brazing and welding. Another example is the development of tennis racket technology where neutrons have the ability to see boron fiber delaminations in a graphite matrix. One major application for neutron radiography is monitoring of cigarette manufacture procedures.

Neutron radiography techniques have been developed and applied for studies of archeological objects and other museum treasures. One technique for paintings is to image the ionizing radiation resulting from neutron capture, a method which can reveal hidden layers of the artist’s work and help differentiate forgeries. Forensic science and security system support to complement thermal neutron activation are other areas that are being considered.

Dynamic imaging neutron radiography is being developed for numerous industrial applications. In England cold neutron dynamic imaging was used to study oil flow in operating jet aircraft engines.

Companies in Hungary that design improved absorption and compression refrigerators have used neutrons to study the behavior of lubrication and cooling oil as pressure, temperature, flow rate and other parameters are varied. In France design work on hydrocarbons (HFC) to replace the stratospheric polluting chloro-fluoro-carbons (CFC) in compressor type automotive air conditioner has relied on neutron radiography to evaluate problems such as non miscible oil-liquid refrigerant. The liquid flow, liquid evaporation, and thermal exchanges are seriously altered by any oil separation. Also oil accumulation in the evaporator endangers the lubrication of the compressor.

The most extensive work on dynamic imaging neutron radiography is being carried out in Japan. Teams at Musashi Institute of Technology and the University of Tokyo have worked on systems development, and scientists at Kyoto University have studied boiling two-phase flow in narrow channels related to nuclear fusion reactor blanket cooling design. Some of this work has used the Nuclear Safety Research Reactor (NSRR) at JAERI in pulsed mode with a video camera operable to 1000 frames per second. Studies include gas-solid spouted beds such as are used for driers of food grains, and liquid solid spouted beds that have application in high heat transfer systems. A team at Kobe University has studied multiphase flow and void fraction in water-aluminum systems, and visualization of streak lines for thermal hydraulic design of lead-bismuth eutectic.

HIGH TECHNOLOGY APPLICATIONS

A typical block valve has a body of aluminum with telescoping slip rods of steel and a set of nylon gaskets or o-rings. Neutron radiography, unlike X-rays, can reliably show if a vital "o" ring is missing. All pilot ejection mechanisms in military aircraft are inspected using neutron radiography. One part is the explosive train encased in silver where any gap could cause a failure. Other critical pyrotechnical items are inspected for missing explosive charge. Rockets used for communications or military satellites can require neutron radiography on over 50 different items for each launch. The explosive bolts are one example were both neutron radiography and X radiography are needed to provide a thorough examination. The complementary
nature of N-ray and X-ray is also apparent for the probing of detonators and fuses. Automotive air bag mechanisms and commercial aircraft escape devices are examples of items that must work on demand, and therefore could justify both N-ray and X-ray inspection. For many detonators and relays a comparison of X-ray, thermal N-ray, and cold neutron radiograph has proven valuable.

SUMMARY

Neutron radiography methods that are being pioneered at the Japanese Atomic Energy Research Institute, and that will be visited as part of this conference, include: (1) thermal and epithermal neutron, gamma insensitive imaging, for development of power reactor nuclear fuels; (2) thermal neutron radiography for direct film imaging of non-radioactive objects; (3) cold neutron radiography for evaluation of non-radioactive objects; (4) pulsed reactor applications for neutron radiography requiring very high flux; (5) video methods of electronic imaging for dynamic studies with neutron radiography; (6) computed tomography methods for neutron radiography of either radioactive or non-radioactive objects.

The techniques can help meet needs in fields as important and diverse as energy supply, transport, food and shelter, medicine, consumer products, and various high technologies. In each case two distinct roles should be considered: (1) nondestructive testing on the finished product and (2) use of neutron radiography to help design improved products.

REFERENCES

USES OF REACTOR NEUTRONS for STUDYING the MICROCOMPOSITION of MATERIALS*

R. E. Jervis
SLOWPOKE Nuclear Reactor Facility, and Dept. Chem. Eng.,
University of Toronto, Toronto, Canada

ABSTRACT

Reactor neutrons constitute excellent 'probes' for exploring and measuring a wide range both of minor and trace constituents in solids and liquids with high sensitivity because of their transparency in materials. Nondestructive neutron prompt-gamma analysis (PGA) utilizing either cold or thermal neutrons, such as at JRR-3M, is compared and contrasted to the more common (delayed) instrumental neutron activation analysis (INAA) and epithermal NAA. Clearly PGA offers high sensitivity for selected elements: B, H, Cd and REE's in suitable matrices, and is therefore, complementary to INAA which is not as useful for them, or for Ni, Sn, Fe, C or N.

Recent INAA applications in our laboratory that demonstrate some of the uniqueness of neutron methods include use of epithermal neutrons for small biological specimens to measure Cd, K, As, Zn and, multielemental INAA for environmental pollution studies. The latter involves large data sets of multielemental concentrations which are subjected to statistical multivariant factor analysis to reveal unknown or unsuspected quantitative relationships among groups of trace constituents. These patterns, or 'factors' are shown to be uniquely related to pollution sources and can be utilized to compute the relative source contributions at a given receptor site.

INTRODUCTION:

For more than 40 years, neutrons have proven very useful for studying the microcomposition of materials. In earlier years the methods, although sensitive, were quite primitive as were the simple $\beta$- and $\gamma$-detectors used for the measurement of those radionuclides induced in materials by neutron activation. Most often tedious radiochemical procedures had to be developed or modified to permit selective analysis of different components. However the increasing availability of reactor, accelerator-produced and radioisotope-excited neutrons of energies from $eV$ to MeV has permitted a significant growth both in neutron methods and their uses. Neutron fluxes within reactor cores, their moderator blocks and tanks, in internal and external neutron beams, neutron sources in space and in mobile lunar explorers, even neutron pulses in underground caverns at nuclear explosions, have all been utilized for measuring low concentrations either of a few selected elements or a wide range of microelements. Notable achievements of neutron methods have been: accurate calibrations of reference materials, lunar rocks, ultrapure materials, and rare earth elements (REE) in rocks and meteorites. The neutron-based methods involved, several of which are discussed in this conference include: neutron activation analysis (NAA) and special adaptations of it: (INAA) instrumental, (ENAA) epithermal, (RCAA) radiochemical, (PCNAA) preconcentration, (SSNAA) substoichiometric, (CNA) cyclic; prompt (capture) gamma analysis (PGA); neutron diffraction and radiography, and,

* (Paper for presentation to the 5th Symposium: Advanced Nuclear Energy Research, JAERI, held in Mito, Japan, March, 1993)
nuclear track analysis. Each neutron method has its advantages and applicability, often complementary to each other, but few establishments have all techniques available.

As to the practicality of using neutrons for material analyses, this has often depended and been limited by access to neutron facilities installed for other purposes. Scientists interested in microanalysis had to share facilities established primarily for neutron physics and which have been summarily shut down because of escalating costs when the needs of nuclear physics have changed. Nuclear analytical uses of neutron beams and thermal columns have had to fit in between lengthy physics experiments. Now, many such facilities have been discontinued worldwide. However, notwithstanding these difficulties in gaining access to suitable neutron sources, unlike the vagaries of nuclear physics research, the capabilities of neutron microanalytical methods and the number and variety of needs for them have continued to grow through each of the past 5 decades. As a consequence, neutron-producing facilities which have been dedicated to analytical uses in different scientific fields and disciplines (as well as neutron physics) have flourished. Of particular note have been the development of low cost, user-oriented mini-reactors of powers 1 MW and lower, typically around 100 KW, as neutron sources for applications. Their simplicity, low cost, inherent safety, day-to-day reliability and neutron flux constancy have encouraged their widespread utilization for studying the microcomposition of materials, e.g. new materials synthesis, microelectronics and super-pure crystals, applied chemistry, environmental, geochemical, archiometric, forensic, clinical and biomedical studies. The US TRIGA, the Canadian SLOWPOKE-2 and their Chinese counterpart, are examples of user-dedicated mini-reactors of which between 100 and 200 are in constant operation around the world, including in developing countries. Although they provide neutrons at orders of magnitude lower fluence than provided by the new JRR-3M facilities, however, they have proved very useful for microanalysis and in certain applications, are advantageous.

ATTRIBUTES OF NEUTRON-BASED ANALYTICAL METHODS

The different neutron methods cited above are not always alternatives but more often are complementary to each other and a research group will often use two such methods for the same materials because, in practice, any one of the neutron methods can only provide a fraction of the compositional information required. (Below, examples are cited in which a neutron beam method such as PGA can very significantly extend the range of components measureable by INAA alone). The challenge to the analysts of the 1990's and beyond and where their wisdom and expertise are required is to choose the 'most appropriate' method to use for the particular material to be measured out of the range of sophisticated and highly developed instrumental analysis techniques available, viz., in addition to the nuclear analytical methods (cited above), a choice needs to be made also among ICP, XRF, AAS, spectrometric, electroanalytical, laser plasma/ablation techniques, and others that are arising.

An important attribute of neutron-based methods is their capability to be applied to sample specimens non-destructively because of neutron transparency and γ-spectrometry. This physically-nondestructive aspect is considered to be quite important in practice for modern analytical techniques for several distinctive reasons: not only to preserve the integrity of the sample for further measurements and for the inherent simplicity of instrumental techniques that
permit replicate measurements and that lend themselves to semi-routine application, to automation and to use by less-qualified laboratory personnel, but also for better precision and accuracy to be achieved. Trace analysis techniques that require prior digestion, fusion or other destruction of the sample are more subject to limitations due to: (i) spurious contamination from handling, from laboratory equipment, from chemical reagents or previous procedures, (ii) uncertain losses during such procedures, (iii) the need to make corrections to the analyte from such sources, and, (iv) the inability to replicate the analysis for exactly the same specimen. Also, when various elements have to be measured sequentially in separate portions of sample, as is the case for many instrumental methods of chemical analysis, there is always a larger combined error in the derived relative concentrations of different elements which is a practical disadvantage when inter-relationships among elements are to be utilized, such as for source identification in environmental studies (see below).

Another attribute of these methods is sensitivity, variously defined as the minimum mass or concentration of analyte that can be measured by a given technique within some acceptable degree of precision, or, the level of analyte that corresponds to 2 to 3 standard deviations of the measurement. While some techniques are limited to a certain concentration sensitivity (regardless of the mass of specimen available for analysis), other methods have an absolute mass sensitivity in nanograms, say. When a method permits a range of samples sizes to be measured, then the concentration sensitivity can be correspondingly increased (improved), within practical limits. On the other hand, charged-particle methods and some instrumental methods such as ICP, AAS, XRF have fixed concentration limits of sensitivity. The relative transparency of neutrons in most matrices makes it possible to bombard specimens which are either quite small or which may be many grams in total mass.

In the remainder of this paper, attributes of neutron-based methods are illustrated by citing examples of microcomposition studies by PGA, ENAA and multielemental INAA, the latter used in conjunction with statistical multivariate analysis.

**PROMPT GAMMA ANALYSIS**

PGA has an inherent advantage for selective, low level analysis because it is an on-line, prompt method of using neutron reactions and responds to different sample components in proportion to their respective n-capture cross-sections and relative concentrations. By comparison, activation methods may detect fewer events since they are dependent not only on the cross-sections but also on exponential radionuclide ‘build-up’ factors which vary with the nuclide half-lives relative to sample bombardment times. However, whereas PGA is limited to suitable sample matrices of low neutron absorption, in conventional NAA, preferential build-up and decay can often be optimized to minimize matrix activation interference. Selective activation and decay for optimizing the determination of particular components can be achieved by using varying activation times and decay intervals to measure short-, medium- and long-lived radionuclides. Such selectivity for desired analytes cannot be achieved in PGA during neutron bombardment. Both methods utilize gamma spectrometry for final resolution of multiple components but the gamma spectra arising in PGA are more complex owing to additional peaks from pair production and annihilation quanta escape phenomena.
Previously, PGA sensitivity was appreciably less than other neutron methods of analysis but, the recent design and installation of cold neutron sources and improved beam guide tubes has increased the neutron fluxes at the sample position to greater than $10^8$ and has decreased interfering background at the detector. The new Compton-suppression BGO/Ge capture-gamma spectrometer has also greatly enhanced the signal/background ratio (by about a factor of 4 for some elements to greater than 10 for others) so that the JRR-3M is now one of the best systems reported.

In Table 1, the sensitivities of the PGA systems at JAERI, NIST, Missouri and ILL (France) are compared using available literature values (of which the results for the first two labs listed above are recent, unpublished results). Absolute detection limits for elements such as B, Cd and Gd are now as low as 1-7 ng. Recent studies by Yonezawa at JRR-3M indicate analysis for these elements down to ppb levels, and, to ppm levels for other elements.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>γ-Energy (keV)</th>
<th>NIST</th>
<th>Missouri</th>
<th>JAERI</th>
<th>ILL</th>
<th>DL (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2223</td>
<td>2.2</td>
<td>2</td>
<td>2.5</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>478</td>
<td>530</td>
<td>760</td>
<td>1480</td>
<td>2700</td>
<td>0.002</td>
</tr>
<tr>
<td>Cl</td>
<td>1165</td>
<td>4.6</td>
<td>1.4</td>
<td>3.4</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>465</td>
<td>0.38</td>
<td>0.17</td>
<td>0.28</td>
<td></td>
<td>5.1</td>
</tr>
<tr>
<td>Cd</td>
<td>558</td>
<td>550</td>
<td>250</td>
<td>250</td>
<td></td>
<td>0.007</td>
</tr>
<tr>
<td>Gd</td>
<td>182</td>
<td>1750</td>
<td>950</td>
<td>980</td>
<td>6900</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Flux (n/cm²-s) | 1.5 x 10⁶ | 5 x 10⁸ | 1.1 x 10⁸ | 1.3 x 10⁸ |
Reference:     | (2)       | (3)     | (4)       | (5)      |

EPITHERMAL NEUTRON ACTIVATION

Epithermal neutrons may be used to advantage for selective determination of those elements with finite resonance-integral cross-sections, particularly when they occur at low concentrations in matrices strongly activated by thermal neutrons, such as soils and minerals, most metals and biological matter. The use of boron or cadmium thermal neutron shields cause a large reprep of thermal-n reactions and allow reactions with epithermal neutrons to be greatly enhanced.

A recent example of the use of epithermal neutrons in our laboratory is the determination of trace cadmium in human bone cores. To be able to measure nanogram
quantities of Cd non-destructively in small (0.01-0.02 g), precious, human bone biopsy specimens is vital because exposure to Cd has been associated with bone abnormalities, however such samples are difficult to obtain from patients and must be preserved intact for histological examination. Because of intense Na, Cl and Ca activation by thermal neutrons, Cd cannot even be detected non-destructively by thermal NAA at normal concentrations of 1-10 μg/g. For this special application, an ENAA method was developed based on bone sample irradiation inside 1 mm Cd metal and B₃C thermal-n shields. Irradiations were done inside the core of the McMaster 5 MW pool reactor at the (higher) 10¹³ thermal flux (1.5-2 x 10¹² epi-th flux) in order to achieve sufficient sensitivity to 0.3 ppm. ‘Advantage factors’ defined as the ratio of ¹¹⁶Cd activity to that of interfering ¹⁸Na with and without the two kinds of epithermal shields, were measured to be 12.2 and 16.7⁶.

MULTIELEMENTAL INAA ANALYSES WITH MINIREACTOR NEUTRONS

For studies in which it is desirable to measure as many as possible components in a single sample specimen, INAA is a preferred neutron technique. (Although INAA examples cited below have been carried using a Canadian minireactor of 20 kW power, φ_max=10¹², similar measurements can be made using high flux reactors such as JRR-3M although with some limitations). An on-line method such as PGA is also inherently multielemental but it is limited in practical applicability to selected elements of high σ in low σ matrices and to elements whose capture gammas fall in a suitable region of the sample spectrum. Typical PGA studies report 5-10 elements measureable in particular sample types and these are often elements such as B, Pb, N which are not readily measureable by other nuclear analytical methods. By designing non-destructive INAA techniques for sequential detection of short, medium and long-lived activation products as many as 35-40 trace elements can be determined in a single sample.

Extensions of these neutron-based techniques in special studies such as the well-known analyses of lunar rocks have resulted in the determination of more than 60 elements. Clearly, for that type of study, because of the uniqueness of the ‘precious’ lunar samples and curiosity about their composition and origin, it was important to determine as many elements as possible. Certain environmental studies such as the examples below also require such multielemental analyses.

In recent work in our laboratory⁷ and others⁸ it has proven useful to adapt INAA methods supplemented by another complementary nuclear method such as, in our laboratory, PNAA (photonuclear activation) and proton PIXE to be able to determine more than 30 elements semi-routinely in large sets of environmental samples. The reasons for carrying on such comprehensive environmental analyses can be explained as follows: while only a relatively few chemical elements can be classified as ‘environmentally important’ owing to their known toxicity to humans, their persistence in the environment and tendency to incorporate in pathways of human exposure, other components measureable in the environment have been shown to be useful as key indicators, or ‘markers’ characteristic of particular sources of environmental contamination. Because concentration co-relationships among marker elements stemming from the same sources are not always known or predetermined, they have to be derived from
Table 2: Elemental Concentrations in Airborne Particulate Matter (1a in ng/m³) and in Ash samples (1b in ppm) from Hospital and Municipal Incinerators

<table>
<thead>
<tr>
<th>Element</th>
<th>Site 1 1a</th>
<th>Site 2 1a</th>
<th>Suburban 1a</th>
<th>Hospital Inc. Ash (1b)</th>
<th>Municipal Inc. Ash (1b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>5.3</td>
<td>4.2</td>
<td>0.56</td>
<td>160</td>
<td>85</td>
</tr>
<tr>
<td>Al</td>
<td>2460</td>
<td>1680</td>
<td>600</td>
<td>40200</td>
<td>10900</td>
</tr>
<tr>
<td>As</td>
<td>12.4</td>
<td>9.3</td>
<td>5.3</td>
<td>98</td>
<td>40</td>
</tr>
<tr>
<td>Br</td>
<td>27</td>
<td>42</td>
<td>70</td>
<td>180</td>
<td>120</td>
</tr>
<tr>
<td>Ca</td>
<td>4905</td>
<td>803</td>
<td>2150</td>
<td>25500</td>
<td>43000</td>
</tr>
<tr>
<td>Cd⁺</td>
<td>8.2</td>
<td>6.0</td>
<td>--</td>
<td>680</td>
<td>42</td>
</tr>
<tr>
<td>Ce</td>
<td>2.7</td>
<td>1.8</td>
<td>--</td>
<td>34</td>
<td>78</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>4300</td>
<td>7800</td>
<td>2340</td>
<td>99000</td>
<td>80000</td>
</tr>
<tr>
<td>Co</td>
<td>1.12</td>
<td>.82</td>
<td>0.45</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Cr⁺</td>
<td>32.0</td>
<td>27</td>
<td>7.5</td>
<td>2422</td>
<td>1330</td>
</tr>
<tr>
<td>Cs</td>
<td>&gt; 2.7</td>
<td>2.8</td>
<td>--</td>
<td>3</td>
<td>0.76</td>
</tr>
<tr>
<td>Cu</td>
<td>2370</td>
<td>1829</td>
<td>740</td>
<td>2.2</td>
<td>--</td>
</tr>
<tr>
<td>Fe</td>
<td>1640</td>
<td>1230</td>
<td>640</td>
<td>36500</td>
<td>52000</td>
</tr>
<tr>
<td>Hf</td>
<td>&gt; 0.42</td>
<td>--</td>
<td>--</td>
<td>2.6</td>
<td>6.8</td>
</tr>
<tr>
<td>I</td>
<td>1.4</td>
<td>&gt; 0.8</td>
<td>3.2</td>
<td>6.8</td>
<td>25</td>
</tr>
<tr>
<td>K</td>
<td>550</td>
<td>1100</td>
<td>--</td>
<td>32050</td>
<td>--</td>
</tr>
<tr>
<td>La</td>
<td>1.2</td>
<td>2.4</td>
<td>1.5</td>
<td>13</td>
<td>34</td>
</tr>
<tr>
<td>Mn</td>
<td>115</td>
<td>278</td>
<td>34</td>
<td>1260</td>
<td>4300</td>
</tr>
<tr>
<td>Na</td>
<td>625</td>
<td>1890</td>
<td>1520</td>
<td>18200</td>
<td>14500</td>
</tr>
<tr>
<td>Ni</td>
<td>23</td>
<td>26</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Pb</td>
<td>210</td>
<td>330</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Sb⁺</td>
<td>6.4</td>
<td>4.9</td>
<td>1.4</td>
<td>750</td>
<td>270</td>
</tr>
<tr>
<td>Sc</td>
<td>0.37</td>
<td>0.38</td>
<td>--</td>
<td>5.6</td>
<td>10.4</td>
</tr>
<tr>
<td>Se</td>
<td>2.27</td>
<td>2.90</td>
<td>3.3</td>
<td>66</td>
<td>3.4</td>
</tr>
<tr>
<td>Ti</td>
<td>150</td>
<td>230</td>
<td>64</td>
<td>21000</td>
<td>32000</td>
</tr>
<tr>
<td>V</td>
<td>16.8</td>
<td>91.8</td>
<td>5.9</td>
<td>15.4</td>
<td>135</td>
</tr>
<tr>
<td>W</td>
<td>0.75</td>
<td>&gt; 0.43</td>
<td>--</td>
<td>12.4</td>
<td>16</td>
</tr>
<tr>
<td>Zn⁺</td>
<td>434</td>
<td>330</td>
<td>108</td>
<td>18000</td>
<td>10800</td>
</tr>
</tbody>
</table>

Hospital incinerator marker elements
measured data sets by means of multivariate correlational analysis. For this to work it is vital to use a reliable multi elemental analytical technique such as INAA that can yield concentration data for multiple components relatively free from random or uncontrolled errors.

Examples of key marker elements which are characteristic of particular (and, common) air particulate sources are: V, Se (oil and other fossil fuels); Cl, Cr, Sh, Cd, Zn (incinerators); Mn, Br, Zn (motor vehicles); Al, Fe, Ba, REE's (soil dust). These marker elements can be confirmed by direct analysis of stack emission samples or residual ashes from combustion plants, industrial sources or incinerators.

In Table 2 are listed mean concentrations and ranges for about 30 elements in ambient aerosols and residual ashes from two hospital incinerators, in ng/m³ and µg/g units respectively, as determined by a combination of INAA and PIXE. The latter method was used on the same samples mainly to extend the range of elements measureable by INAA alone, such as Pb,Cd,Ni,Se,S. These were done using neutrons in the U. of Toronto SLOWPOKE-2 mini-reactor and 1.5-3 MeV protons at the U. of Guelph accelerator. Repeated sampling (n=35 and 26) at the 2 sites was done using Hi-Vol air samplers (0.3 m³/min) during 12 hours periods extending over 4-5 months periods. Sampling was repeated not only to obtain good mean aerosol concentrations averaged over different wind speed and directions and different source emission days, but also, because statistical analysis was done on the variances of individual elements for the entire concentration data set.

Notable from the table (as indicated by **) both for the aerosols at the two sites and for the hospital incinerator ash were elevations of Ag,Cd,Cl,Cr,Sb and Zn characteristic of high-temperature combustion. By comparison, the municipal incinerator did not show such elevations consistently although high levels of Ag,Cl,Cr,Fe,Ti,V and Zn were evident.

As mentioned, statistical analysis of variance among the elements' concentrations can reveal inter-relationships among small groups of elements, called 'factors', which are caused because such elements are emitted in characteristic ratios from the same particular sources and tend to exhibit the same positive or negative fluctuations as a function of meteorological factors and temporal variations in emission rates on different sampling days. The STATGRAPHICS\(^1\) software was employed for multivariate factor analysis as illustrated in the Figure. A matrix diagonal rotation procedure: 'Varimax' was used to minimize insignificant correlations of individual elements in factors, causing the (so-called) factor loadings either to be large approaching unity, or to be small. Elements that fall into particular factors with loadings greater than 0.3-0.5 are considered to be significantly correlated with that group of elements. Of the 17 elements included in Table 3 for site 1 results, all have a significant loading in at least one factor (most are >0.6) and 5 factors have been included. For example, Al has a loading of 0.93 in factor 1, attributable to soil dust but in other factors its loadings are very low positive or negative values. It is seen how the Varimax procedure produced factors loadings from 0.4-1 or else low values. This simplifies decisions as to which elements are included in the different factors (Table 4). Each factor is comprised of 3 to 5 elements plus a wind direction as shown for the hospital incinerator factor.

\(^1\)STATGRAPHICS is the name of a software statistical package provided by STSC Inc., Rockville, MD, 20852
Figure 1
Statigraphic Approach to Factor Analysis

DATA MANAGEMENT
\( \searrow \) Data Input
\( \swarrow \) MULTIVARIATE METHODS
\( \searrow \) FACTOR ANALYSIS
\( \swarrow \) Data File
\( \searrow \) TYPE OF ROTATION
\( \swarrow \) Principal Components
\( \swarrow \) Communality
\( \swarrow \) Eigenvalue
\( \swarrow \) Percentage of Variance
\( \searrow \) FACTOR EXTRACTION
\( \swarrow \) FACTOR MATRIX

Table 3: Varimax Rotated Factor Loadings for Site 1

<table>
<thead>
<tr>
<th>Element</th>
<th>Factor 1 (soil)</th>
<th>Factor 2 (hospital)</th>
<th>Factor 3 (cement)</th>
<th>Factor 4 (vehicles)</th>
<th>Factor 5 (oil/coal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.93</td>
<td>0.08</td>
<td>0.12</td>
<td>-0.08</td>
<td>-0.23</td>
</tr>
<tr>
<td>Fe</td>
<td>0.65</td>
<td>-0.34</td>
<td>0.76</td>
<td>-0.29</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.32</td>
<td>-0.11</td>
<td>0.21</td>
<td>0.72</td>
<td>-0.31</td>
</tr>
<tr>
<td>Ca</td>
<td>0.22</td>
<td>-0.21</td>
<td>0.99</td>
<td>-0.23</td>
<td>0.01</td>
</tr>
<tr>
<td>Sc</td>
<td>0.96</td>
<td>-0.32</td>
<td>0.08</td>
<td>-0.18</td>
<td>0.23</td>
</tr>
<tr>
<td>Pb</td>
<td>0.14</td>
<td>0.30</td>
<td>-0.32</td>
<td>0.84</td>
<td>-0.21</td>
</tr>
<tr>
<td>Si</td>
<td>0.58</td>
<td>-0.23</td>
<td>0.93</td>
<td>-0.32</td>
<td>-0.24</td>
</tr>
<tr>
<td>Br</td>
<td>0.12</td>
<td>0.08</td>
<td>-0.28</td>
<td>0.97</td>
<td>-0.21</td>
</tr>
<tr>
<td>Zn</td>
<td>-0.31</td>
<td>0.38</td>
<td>-0.20</td>
<td>0.19</td>
<td>0.39</td>
</tr>
<tr>
<td>La</td>
<td>0.80</td>
<td>-0.12</td>
<td>-0.03</td>
<td>-0.18</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl</td>
<td>0.08</td>
<td>0.92</td>
<td>-0.21</td>
<td>0.09</td>
<td>-0.28</td>
</tr>
<tr>
<td>As</td>
<td>-0.01</td>
<td>0.86</td>
<td>-0.18</td>
<td>-0.10</td>
<td>-0.11</td>
</tr>
<tr>
<td>Sm</td>
<td>0.72</td>
<td>-0.09</td>
<td>0.01</td>
<td>0.22</td>
<td>-0.32</td>
</tr>
<tr>
<td>Sb</td>
<td>-0.12</td>
<td>0.62</td>
<td>-0.23</td>
<td>0.16</td>
<td>-0.15</td>
</tr>
<tr>
<td>S</td>
<td>-0.21</td>
<td>-0.31</td>
<td>0.05</td>
<td>0.02</td>
<td>0.96</td>
</tr>
<tr>
<td>Cd</td>
<td>0.13</td>
<td>0.93</td>
<td>-0.07</td>
<td>-0.21</td>
<td>-0.02</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.13</td>
<td>0.86</td>
<td>-0.18</td>
<td>-0.10</td>
<td>-0.11</td>
</tr>
<tr>
<td>South</td>
<td>0.13</td>
<td>0.82</td>
<td>-0.12</td>
<td>0.02</td>
<td>-0.05</td>
</tr>
<tr>
<td>Southwest</td>
<td>0.08</td>
<td>-0.21</td>
<td>0.93</td>
<td>-0.32</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*hospital marker elements
Table 4: Rotated Factor Pattern For Site 1

<table>
<thead>
<tr>
<th>F1(Soil)</th>
<th>F2(Hospital)</th>
<th>F3(Cement)</th>
<th>F4(Vehicle)</th>
<th>F5(Sulfate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc (0.96)</td>
<td>Cd (0.93)</td>
<td>Ca (0.99)</td>
<td>Br (0.97)</td>
<td>S (0.96)</td>
</tr>
<tr>
<td>Al (0.93)</td>
<td>Cl (0.92)</td>
<td>Sw* (0.93)</td>
<td>Pb (0.84)</td>
<td>As (0.82)</td>
</tr>
<tr>
<td>La (0.80)</td>
<td>Ag (0.86)</td>
<td>Si (0.76)</td>
<td>Mn (0.72)</td>
<td>Zn (0.39)</td>
</tr>
<tr>
<td>Sm (0.72)</td>
<td>Sb (0.62)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe (0.65)</td>
<td>Zn (0.38)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South (0.82)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*SW = southwest wind

Eigenvalues for the first 11 possible factors provided for this data set by STATGRAPHICS are shown in Table 5, also, the fraction of total variance accounted for by each factor. The 5 factors chosen all had eigenvalues greater than unity, accounted for more than 87% of all the variance in the data set (Table 5) and all element loadings are quite high. Obviously, factors other than the first 5 are weak contributors although one or more of them may correspond to real (though, unidentified) sources. The five factors have been identified independently by measurements of source samples and by the literature to be: wind-entrained soil particles (factor 1); hospital incinerator emissions (factor 2); dust particles from cement use (factor 3); motor vehicle emissions and historical contamination of mobile surface deposits (factor 4); and, a combustion source (factor 5). The latter source also exhibited small particle Se, marker for coal combustion, and V, marker for oil combustion, in particle-size separated samples, and could include aerosol transported over long distances from industrialized cities of the mid-west U.S. Similar findings resulted from factor analysis of site 2 data which was divided into coarse (>2 μm) and fine (<2 μm) particles, except that a 6th factor was also resolved.

Table 5: Eigenvalue Analysis of Correlation Matrix for Site 1 Data

<table>
<thead>
<tr>
<th>Factor No.</th>
<th>Eigenvalue</th>
<th>Percent Variance</th>
<th>Cumulative % variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.09</td>
<td>35.2</td>
<td>35.2</td>
</tr>
<tr>
<td>2</td>
<td>2.34</td>
<td>27.1</td>
<td>62.3</td>
</tr>
<tr>
<td>3</td>
<td>1.80</td>
<td>14.2</td>
<td>76.5</td>
</tr>
<tr>
<td>4</td>
<td>1.28</td>
<td>6.1</td>
<td>82.6</td>
</tr>
<tr>
<td>5</td>
<td>1.01</td>
<td>4.7</td>
<td>87.3</td>
</tr>
<tr>
<td>6</td>
<td>0.73</td>
<td>3.9</td>
<td>91.2</td>
</tr>
<tr>
<td>7</td>
<td>0.62</td>
<td>2.8</td>
<td>94.0</td>
</tr>
<tr>
<td>8</td>
<td>0.48</td>
<td>2.5</td>
<td>96.5</td>
</tr>
<tr>
<td>9</td>
<td>0.32</td>
<td>1.8</td>
<td>98.4</td>
</tr>
<tr>
<td>10</td>
<td>0.21</td>
<td>1.4</td>
<td>99.8</td>
</tr>
<tr>
<td>11</td>
<td>0.07</td>
<td>0.2</td>
<td>100</td>
</tr>
</tbody>
</table>
These source identifications which were possible through factor analysis of the large concentration data set (obtained by INAA and PIXE) demonstrate the value of having used neutron methods for this type of research. The fact that so many strong correlations (viz. high factor loadings) were found in this data is a tribute to the reliability and relative freedom from uncontrolled errors in the aerosol concentrations. That this was due to the INAA method was further substantiated by a separate controlled study in which both INAA and XRF analyses were performed on the same set of air filters from steel-making Canadian cities. While the INAA concentration data revealed 4 factors with good loadings, including a distinct steel factor, the XRF results did not yield good correlations, indicative that there were many errors in the XRF filter measurements; also, some elements were barely detectable by XRF.

AIR POLLUTION SOURCE APPORTIONMENT BY INAA

Once the major sources of air pollution at a given receptor site have been identified by factor analysis, a chemical element balance computation (CEB) applied to the same aerosol data can quantitatively apportion relative contributions of each of the identified sources to the ambient aerosol at the receptor site. This CEB model assumes that the concentrations of any element ‘i’ at the site is a linear sum of the contributions of that element from ‘j’ sources:

\[ a_i = b_{ij} \cdot c_j \]

where: \( a_i \) = concentration of ‘i’ th element at receptor site,
\( b_{ij} \) = mass fraction of ‘i’ th element in the mass from source ‘j’ collected at receptor,
\( c_j \) = ratio of mass contributed by source ‘j’ to total collected mass

and this calculation leads to a matrix solved by least squares regression separately for each air filter, the results being averaged over all filters to yield a mean contribution of each aerosol source at the receptor site. In Table 6: are listed the relative contributions of each of six identified sources to the total air particulate at the two hospital sites: while their incinerators contributed 22 and 36%, respectively to total aerosol in the vicinity, their contributions to particular components were greater: Cd(68%), Cl(74%), Cr(46%), Pb(28%), Sb(60%), Se(48%) and Zn(43%), (results not shown in the table, however).

<table>
<thead>
<tr>
<th>Source</th>
<th>Site 1 (summer)</th>
<th>Site 2 (fine winter)</th>
<th>Site 2 (coarse winter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hospital incineration</td>
<td>22</td>
<td>36</td>
<td>6</td>
</tr>
<tr>
<td>Motor Vehicle</td>
<td>9</td>
<td>24</td>
<td>1.5</td>
</tr>
<tr>
<td>Wind-entrained soil/road dust</td>
<td>55</td>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>Cement from construction</td>
<td>12</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Coal combustion/second.sulphate</td>
<td>2.3</td>
<td>30</td>
<td>n.a.</td>
</tr>
<tr>
<td>De-icing salt</td>
<td>n.a.</td>
<td>n.a.</td>
<td>13.5</td>
</tr>
</tbody>
</table>

— 142 —
SUMMARY

Reactor neutrons are valuable probes for exploring the micro-composition of materials. Compared to other non-nuclear techniques, neutron-based methods such as INAA, ENAA and PGA have the advantages of being non-destructive, selective, sensitive, multielemental and somewhat less error-prone in the hands of experienced and knowledgeable personnel. However it can be asserted, based on much minireactor utilization experience, that INAA can be used quite reliably also by novice analysts from other disciplines who have materials amenable to neutron methods such as archiometry, environmental, geochemical and medical studies. Furthermore, such non-destructive INAA multielemental measurements can be accomplished with large sample suites at unparalleled low costs for trace analyses - of the order of one dollar (US) per analysis.

REFERENCES

(1) C. Yonezawa, "Prompt gamma-ray analysis of elements using cold and thermal neutron beams", Analytical Sciences, (accepted, 1993)


(6) R. Dowlati, R.E. Jervis, ibid, 150 455 (1991)

(7) M.M.C. Ko, R.E. Jervis, "Atmospheric Toxic Metal Contributions From Hospital Incinerators" ibid, 161 159 (1992)

COMMERCIAL APPLICATIONS OF NEUTRON SCATTERING

Michael T HUTCHINGS

National NDT Centre, AEA Technology,
Harwell Laboratory, Didcot, OX11 0RA, U.K.

ABSTRACT

The fact that industry is now willing to pay the full commercial cost for certain neutron scattering experiments aimed at solving its urgent materials-related problems is a true testimony to the usefulness of neutrons as microscopic probes. This paper gives examples of such use of three techniques drawn mainly from our experience at AEA Technology Harwell Laboratory. These are diffraction to measure residual stress, small angle neutron scattering to examine hardening precipitates in ferritic steels brought about by irradiation, and reflectivity to study amorphous diamond layers deposited on silicon. In most cases it is the penetrative power of the neutron which proves to be its best asset for commercial industrial applications.

INTRODUCTION

Industry has made use of the neutron as a microscopic probe for its longer-term, generic, research for many years now. For this type of research, the results of which are openly published, it has obtained access to neutron beam facilities through collaboration with National Laboratory or University scientists, often first subjecting its proposed experiments for a peer review committee’s approval. For its more intensive projects, of partly proprietary nature, industry may join a “Participating Research Team” such as those at the National Institute of Standards and Technology in the USA. It provides funds towards a new instrument and scientists to operate it, however the neutron beams are free in exchange for allowing other scientists use of the instrument for part of its scheduled time. This form of collaboration allows rapid access to the facility, and enables commercially confidential work to be carried out as well as routine experiments which might not receive the approval of a review committee although the results are openly publishable. An alternative route for these latter two types of work, and one which has increased markedly during the past decade for short and medium termed projects, is for industry to simply pay the full commercial cost of hiring the neutron beam, the instrument, and the expert scientists to carry out the work. This paper will concentrate on such fully commercial neutron scattering work. It is often aimed at solving a particularly urgent problem involving safety questions, satisfying regulatory bodies, or the improvement of a product. The examples given will be mainly drawn from our experience on the investigation of solid materials at AEA Technology, Harwell Laboratory, now gained through the purchase of beam time on behalf of our customers at European spallation source and reactor facilities. From the facility’s point of view, industrial commercial work provides an important financial input and political justification. However most facilities will continue to regard the more fundamental research as their principal concern, and utilisation of scattering facilities by industry at — 10% level would appear to be a realistic goal.

Neutron Radiography, a traditional use of neutron beams by industry, and Boron Neutron Capture Therapy, a new development, are described in other talks at this Symposium. Other techniques which should be mentioned are neutron depth profiling and neutron activation analysis which are extensively used. Together with their in-pile use for irradiation, isotope production and silicon
transmutation doping, this range of utilisation makes present-day neutron source laboratories diverse and interesting places.

The reason industry will pay a premium to use the neutron as a probe, rather than the more readily accessible x-ray, is primarily due to its high penetration into most materials. A good statistically averaged property of the sample under investigation is obtained, or a profile of the scattering from a small 'gauge' volume can be studied as a function of its position within the material. Materials may be readily studied under the hostile environmental conditions of temperature or pressure found in production plant, as the neutron penetrates the environmental cell walls with relative ease. The use of isotopic substitution and magnetic scattering helps to identify the source of the scattering, the use of H/D substitution being extensively used by the chemical industry. Compared with the other techniques which neutron scattering often complements, relatively little sample preparation is required.

The principal neutron scattering techniques utilised for commercial work are 1): neutron diffraction to study phase formation, texture and residual stress; small angle neutron scattering (SANS) to study surfactants, polymers and precipitate phases; and neutron reflectivity to study surfaces and interfaces of liquids, polymers, proteins, and solid layers. Examples are numerous but, because of the nature of the work, not often easily quoted. The three cases given below are therefore taken partly from analogous work which is available for publication.

**RESIDUAL STRESS MEASUREMENT USING NEUTRON DIFFRACTION**

The detailed measurement of residual stress fields within components and weldments, which are formed by inhomogeneous plastic deformation or heat treatment such as welding, has been a challenge set by engineers for many years. Macrostress or Type I stress, which varies over distances which are relatively large compared to the grain size, is of prime concern to the engineer. However microstress or Type II stress, which varies on a spatial scale of the order of the grain size, can also give information relevant to the mechanical behaviour of many materials.

The neutron diffraction method of stress measurement 2) closely parallels and complements the X-ray diffraction method. However it enables in-depth measurements to be made on account of the much deeper penetration, by a factor of $10^2-10^4$, of the neutron into most materials. It is now used with confidence worldwide as a nondestructive technique, providing new information for the engineer in an increasing number of applications. The major drawback of the neutron diffraction method is its need of intense neutron beams, available only at a medium or high-flux reactor or at an accelerator-based, usually time-pulsed, neutron source. This limits its use to relatively small portable components, with typical maximum dimension ~50-100 cm. However it can also be used to test computer codes using model samples, to test assumptions made in the use of portable, but usually much more limited, techniques, and to calibrate these techniques for use in the factory or field. The exploration of the finer points of the neutron diffraction technique is providing materials scientists with new insights into the fundamental behaviour of materials under stress.

The basic principle of the method lies in the use of the lattice plane spacing of grains to act as an internal strain gauge throughout the component. The method is illustrated in figure 1 and is discussed here mainly in terms of a reactor based instrument, where modified standard high resolution powder neutron diffractometers are often quite suitable although several facilities now have specially designed instruments dedicated to residual stress measurement. The monochromated beam of wavelength $\lambda$ is defined in direction by a soller slit collimator, or by apertures, to pass over the 'sample axis' about which the detector rotates. The detector counts neutrons scattered through an angle $\phi$, with the scattered beam again defined in direction by a soller slit assembly. Both the beam incident on the sample and the beam entering the detector are defined in area by horizontal and vertical apertures in a neutron absorbing mask, made of cadmium for example. The 'gauge volume' or 'volume sampled' by the diffractometer is defined by the intersection of the incident and scattered beam, as shown in figure 1. A sample placed wholly within this volume will have its average property measured, whereas a large sample may be moved through the gauge volume in order to obtain a profile of a property such as strain.
Figure 1. The principles of strain measurement, showing the definition of gauge volume sampled and the direction of strain measured.

Polycrystalline materials give rise to cones of diffracted neutrons at angles $\phi_{hkl} = 2\theta_{hkl}$ about the incident beam on the sample. The cone of scattering arises from a subset of crystallites or grains in the sample, just those which satisfy Bragg's Law and which are oriented so that the planes are at an angle $\theta$ to the incident beam. We define a scattering vector $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$, where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and scattered neutron wavevectors, of magnitude $|\mathbf{k}| = 2\pi\lambda$, as shown in figure 1.

The detector is scanned through $\phi_{hkl}$ to determine the peak-count angle of the hkl reflection, which, in the case of a large sample, corresponds to the average $d_{hkl}$ of the grains in the gauge volume sampled. Usually a fitting routine using least-squares minimisation is used to determine the angle and angular width of the peak. The average lattice macrostrain in the volume sampled is then given by

$$e_{hkl} = \frac{(d_{hkl} - d_{ohkl})}{d_{ohkl}} = \frac{\cot \theta_{ohkl} - (\phi_{hkl} - \phi_{ohkl})}{2},$$

where $d_{ohkl}$ is the lattice spacing of a 'stress free' sample of the same material composition, and $\phi_{ohkl} = 2\theta_{ohkl}$ the corresponding diffraction angle. The direction in which the strain $\epsilon_{hkl}$ is measured is that of the scattering vector $\mathbf{Q}$. The mean lattice microstrain in the volume sampled is related to the angular peak width, although there may be other contributions.

As the lattice spacing can only change elastically it is an elastic strain which is always measured, but this may be a result of intergranular strains arising from a plastic deformation or thermal treatment of the sample. If an accurate value of $d_\phi$ or $\phi_\phi$ can be measured, the strain determined is absolute. However obtaining a true $d_\phi$ may prove difficult in practice. A sum rule or boundary conditions, after conversion to stress, may be used to define the zero stress reference level.

In order to determine the strain in different directions in the sample, the sample must be rotated accurately about the centre of the gauge volume so that each direction lies along $\mathbf{Q}$. This is often quite difficult to do in practice, and requires extremely careful alignment and centering of the sample. At $\phi = 90^\circ$ the cone of diffracted intensity becomes a plane of scattering, and this is also the optimum scattering angle for definition of the gauge volume.

An alternative to a steady reactor source of neutrons is the pulsed white beam of neutrons given by a spallation source. In this case polycrystalline diffraction is observed at a fixed $\phi$. On most standard powder diffraction instruments $\phi$ is usually $\sim 150^\circ$ to $180^\circ$ to give very good resolution, and time of flight $t$ is used to scan the different lattice planes. The strain is now given by $e = \Delta t/v = \Delta \lambda/\lambda$, where $t = L/v = (\lambda m \hbar)/L$. is the time taken for a neutron with mass $m$ and velocity $v$ to travel a path.
length L, and h is Planck’s constant. The advantage of this method is that strains may be measured from many lattice planes (hkl) at once, and dedicated instruments are now being installed to enable the strain to also be measured in several directions at the same time.

In most cases the strain and stress are triaxial and can be represented at each point in the sample by a strain tensor \( \mathbf{e} \) and stress tensor \( \mathbf{g} \) referred to axes Oxzyz in the sample. At least six measurements of \( \varepsilon(\text{m}^2) \) are therefore necessary to determine the six terms in \( \mathbf{g} \), but clearly the accuracy can be improved if more are made. The simplest directions are those along, and at 45° to, the axes Oxzyz. Having determined \( \mathbf{e} \), the principal strain axes Oxzyz and the principal strains \( \mathbf{e}_i \) along them may be found by diagonalisation. Alternatively, symmetry axes of the sample may be assumed to define the principal axes. The principal internal stresses along these axes are then calculated, assuming an elastically isotropic model with macroscopic Young’s modulus E and Poisson’s ratio \( \nu \). In most materials, the values of E and \( \nu \) are dependent on the lattice planes (hkl) used as the ‘strain gauge’, since the elastic response of each grain to an applied stress is anisotropic. Indeed one needs to determine the ‘neutron elastic constants’ by calibration, using for example a compact stress rig which can be accommodated on a neutron diffractometer.

Typically, for steel a shift in \( \phi \) from that of a stress-free sample of 0.01° at 90° indicates a strain of \( \sim 100 \mu \varepsilon \) or a stress of \( \sim 20 \text{ MPa} \). Accuracy in measurement of 0.005° is usually obtained by peak profile fitting using a computer. Practical path lengths, that is of the total incident plus diffracted beams, in steel and in aluminium are typically 50 and 100 mm respectively, for volumes sampled of 27 mm³.

The ability of the neutron diffraction technique to measure the through-thickness strain in each phase of a two-phase material is illustrated by recent work at Harwell Laboratory for the UK Department of Trade and Industry, carried out as a part of a programme to establish suitable mechanical testing procedures for metal matrix composites (MMC’s). Of specific interest is the effect of residual stresses on crack propagation during fracture toughness tests, when crack front curvature might invalidate the test. All MMC’s will exhibit average mismatch stresses, often termed microstresses, due to the unequal contraction coefficients of the matrix and strengthening particles on cooling after formation. However subsequent heat or mechanical treatments may introduce additional macrostresses and it is these which can affect the crack tests. In order to assess their magnitude a plate of BP217 Al/SiC composite which had been subjected first to an anneal at \( \sim 400^\circ \text{C} \) to remove residual macrostress formed during formation, followed by a ‘T4’ heat treatment consisting of heating to \( \sim 505^\circ \text{C} \), at which temperature it was held for approximately one hour, and then a rapid cold water quench and natural age.

![Figure 2. The variation of three principal strain components, as measured using aluminium matrix Bragg reflections (111) for \( e_x \) and \( e_y \), and (022) for \( e_z \), through the thickness of a quenched Al/SiC MMC plate.](image)
The macrostresses introduced by this treatment were investigated by measuring the strains using the $\text{Al}(111)$, $\text{Al}(002)$, and $\text{SiC}(111)$ reflections. Two $\text{Al}$ reflections were required because of texture in the matrix, probably caused by previous rolling. The through-thickness strains measured are shown in figure 2. The data show directly for the first time the expected parabolic variation due to the rapid quench, with compressive strain near the surface and tensile in the centre. The strains measured in the two phases were converted to stress, assuming that the principal axes were those of the plate and that the small anisotropy in the elastic constants could be neglected. The resulting stresses show a similar variation to the corresponding strains. As expected, overall the stress in the $\text{Al}$ phase is more tensile than in the $\text{SiC}$ phase. However a simple separation of these stresses into macrostress, which might be expected to be the same in each phase, and microstress, showed the latter to exhibit some anisotropy rather than the constant level which would arise from mismatch stress. This indicates that the effect of the heat treatment on the macrostress must be included. It is clear from the results that the parabolic macrostress will cause curvature of a fatigue crack front which is parallel to the direction of stress variation.

**SANS OF IRRADIATION INDUCED PRECIPITATES IN REACTOR PRESSURE VESSEL STEELS**

SANS gives important information on the size, shape, volume fraction and, in some cases, composition, of inhomogeneities of size $\sim 1 - 500 \text{nm}$ in a material. If there is a range of size of inhomogeneities the volume fraction size distribution can be determined. It can be sensitive to volume fractions as low as $1 \times 10^{-5}$. SANS attracts more commercial users than any other neutron scattering technique, particularly from the oil and chemical industry. However the example we shall give is one of importance to the safety considerations of the Nuclear Industry. Many power reactors in Europe and the USA are now over 30 years old, and provide increasingly cheap electricity as their capital cost has been paid off. However in considering their life extension the long-term effects of irradiation and temperature on the mechanical properties of key components must be carefully assessed. In the UK the submerged-arc weldments used to join the sub-sections of the pressure vessel of Magnox reactors are of particular concern, as they show the highest effects of irradiation. The ferritic steels used contained copper in solid solution, which under the effects of irradiation diffuses to form Cu-rich precipitates. Although these increase the yield strength they also increase the brittle-ductile transition temperature. These effects are assessed by regular examination of test-coupons of ferritic weld material which have been placed in areas of higher irradiation than the vessel itself so that future problems can be predicted. The coupons, and samples cut from the actual pressure vessel itself, are examined by a range of mechanical and microscopic techniques. SANS in conjunction with transmission electron microscopy (TEM) and atom-probe field ion microscopy (AP/FIM) provides important data for a micro-mechanical model of the hardening process.

The basic SANS macroscopic cross-section is given by:

$$d\Sigma/d\Omega = \sum_k \left[(\rho_{bd} - \rho_{bm})^2\right] C_k V_k |F_k(Q)|^2,$$

where $C_k$ is the volume fraction of inhomogeneities (e.g. precipitates) of volume $V_k$ and structure factor $F_k(Q)$ with average nuclear scattering length density $\rho_{bd}$, in a matrix of scattering length density $\rho_{bm}$. Here the scattering length density is given by the sum of the product of the number of each type of atom per unit volume times its bound scattering length. For unpolarised neutrons and no applied field there is an additional contrast term $\left[(2/3)(\rho_{md} - \rho_{mm})^2\right]$ in the square brackets, where $\rho_{md}$ and $\rho_{mm}$ are the average magnetic scattering densities of the defect and matrix. For chemical applications $\rho_{bd}$ or $\rho_{bm}$ can be changed by isotopic substitution, and in the case of ferritic metals the magnetic term may be changed by the application of magnetic field, in order to help identify the nature of the inhomogeneities. Since it is only the component of magnetisation perpendicular to $Q$ which scatters neutrons, by applying a field one can use the ratio
\[ A = \frac{[d\Sigma /d\Omega_\perp] [d\Sigma /d\Omega_\parallel]}{[(\rho_{bd} - \rho_{bm})^2 + (\rho_{md} - \rho_{mm})^2] / [(\rho_{bd} - \rho_{bm})^2]} \]

to help identify the precipitate. For example pure Cu precipitates would give \( A = 12 \), whereas voids would give \( A = 1.4 \).

![Graph showing volume fraction vs diameter for different conditions.](image)

Figure 3. Volume fraction - particle size distribution of precipitates in unirradiated and irradiated (911 x \(10^{-5}\) dpa at 165°C) mild steel submerged-arc weld material, showing the increase in the volume fraction of precipitates of ~2nm on irradiation.

In work carried out for the UK nuclear industry, samples coupons of ~10 x 10 mm\(^2\) area and ~2mm thick have been examined before and after irradiation. The high sensitivity required is attained through low background, and by elimination of air and window scattering in the instrument. The composition of the precipitates is determined by a combination of the SANS cross section and of FEGSTEM-EDX analysis. Analysis is based on the use of the maximum entropy method to fit the precipitate size distribution assuming spherical particles. The results of a typical experiment are shown in figure 3, where the irradiation clearly produces an increase in precipitates of ~15nm size. The best fit to the data give \( A \sim 2.3 \), suggesting a composition 75Cu25Mn (at %), which is consistent with the TEM results. SANS gave the first indication of such small defects, which change from coherent to incoherent under increasing irradiation but do not increase in size. The technique readily gives a good average precipitate size distribution, and this is used in the model together with a matrix damage term incorporating dislocation loop and void formation to successfully predict the change in yield stress and transition temperature.

**NEUTRON REFLECTIVITY FROM SOLID SURFACES**

The specular reflection of neutrons, used extensively in neutron beam instrumentation such as neutron guides and polarisers, is currently one of the fastest growing neutron scattering techniques, with reflectometers installed or planned at most neutron facilities.

As the neutron refractive index, given by

\[ n = \left[ 1 + \frac{\lambda^2 N b}{2\pi} + i\frac{\lambda N \sigma_a}{4\pi} \right] \]

is slightly less than unity for most materials, total external reflection occurs at an air-solid surface. Here \( N \) is the number of atoms per unit volume of bound scattering length \( b \) and absorption cross section \( \sigma_a \). The critical glancing angle \( \theta_c \) is given by \( \cos \theta_c = n \), so that \( \theta_c = \lambda (N b/\pi)^{1/2} \). At fixed \( \lambda \) for glancing angles \( \theta > \theta_c \) the reflectivity \( R(\theta) \), falls off in a manner determined by the profile of the
refractive index n(z), or, equivalently, the scattering length density ρ(z) (ρ = Nb) as a function of the distance z beneath the surface. Using a time-of-flight reflectometer it is R(λ) which is measured at fixed θ. R(θ) or R(λ) are usually converted to R(Qz) which may be related by a Fourier Transform to dp(z)/dz. However there are seldom sufficient data to effect such a transform directly. The material is usually modelled using the method of Abeles in which it is split into a number of uniform layers of different ρ with interfaces which can be rough or diffuse. The reflectivity is then given by a ratio of the elements of a matrix formed from a product of 2 x 2 matrices which describe each interface. The specular reflection R(Qz) from a perfect surface between air and a uniform material is described by Fresnel's law. The measurement of neutron reflectivity can therefore give information on the density or composition at the surface, the thickness, up to ~500nm, of any deposited layers, and the roughness of the external surface and of the interfaces. A profile of composition can be modelled by a series of layers. The resolution of the instrument must be included as a parameter in the data analysis and the diffuse off-specular intensity has to be subtracted. This diffuse reflectivity is a further source of information on the correlations in roughness of the surface, and of the interfaces. High sensitivity and low background are necessary to measure diffuse reflectivity, and the analogous x-ray reflection technique for which, due to the much higher available flux, R(Qz) can be measured over 8 or 9 orders of magnitude may give advantage over the neutron technique which usually cover a maximum only 5 to 7 orders. Indeed x-ray reflectivity data often complement neutron data, since similar expressions for the reflectivity hold with b replaced by Zλ0, where λ0=8π/λ=mc².

It is the ability to change the reflectivity by isotopic substitution which gives the neutron technique a special advantage to the chemical industry for the study of polymer and surfactant surfaces and it is in this area that most of the commercial work at ISIS, for example, has been carried out. The availability of longer wavelengths, lower absorption, magnetic scattering to study magnetic films, and the independence of scattering length b on Z can lend an advantage to neutrons over x-rays for the study of solid surfaces. This is the area which has been explored at AEA Technology Harwell Laboratory, for the characterisation of ion implanted metals, oxidation layers on silicon, and diamond-like carbon layers on silicon. The latter case will be briefly described as an example 7).

There has recently been considerable interest in depositing hard diamond-like carbon (DLC) layers on materials for increased wear resistance, and in other uses for devices such as infra-red windows. The layers are formed in several ways, in the case chosen a sample of amorphous DLC

![Graph](image)

*Figure 4. Neutron reflectivity profile from an amorphous carbon layer on a silicon wafer. The experimental points taken using the TAS8 reflectometer at Risa, are fitted by the theoretical profile shown as the solid line 7).*
formed by evaporation of a volatile oil onto a silicon wafer under nitrogen ion bombardment. It has been examined by reflectivity to characterise the layers, particularly with regard to hydrogen content, in order to optimise the formation process. Measurements were made using the TAS8 diffractometer at Risø National Laboratory with an incident wavelength of ~4Å and a configuration in which vertical apertures of 1 mm width were placed ~650 mm apart on both the incident and reflected arms of the diffractometer. The detector arm and sample, with its surface in the vertical plane, were rotated away from the straight through position in the ratio 2:1 to give the reflectivity curve as shown in figure 4. These data have been analysed using the Abeles method to give the layer thickness of 1420 Å, a uniform scattering length density of 5.16x10^-6 Å^-2, a surface roughness of 24 Å and an interfacial roughness of 54 Å. The same sample was also studied by x-ray reflectivity, and a combination of the two scattering length densities used to yield a carbon density of ~2 g cm^-3, lower than the ideal diamond density of 3.6 g cm^-3, and a hydrogen content of 28 atomic%. It is clear that such information, which may be obtained in 30 min or less at the most intense spallation sources, can provide important information for the development of processes of surface layer or thin film formation.

CONCLUSIONS

Industry is willing to pay the full commercial cost of using neutron scattering techniques to solve their urgent materials-related problems when unique information can be obtained. Although the relatively low flux of neutron beams can mean that data are acquired slowly, some experiments, notably SANS and neutron reflectivity, may take less time to carry out than required for the sample preparation, alignment and inspection using other more common techniques. Usually the neutron results will be used in conjunction with those from other techniques or from theoretical models. For the scientist carrying out this work the measurements required can often present a challenge equal to, or even greater than, that of more academic research. Examples have been given using the three techniques which are currently most used by industry: diffraction for residual stress measurement, SANS, and the rapidly growing reflectivity technique. Diffraction is also used by industry to measure texture, phase analysis and structures of new compounds, while the other two techniques have wide application in the chemical and pharmaceutical industries. With the rapid improvement in neutron sources, and in instrumentation and data analysis, there is no doubt that commercial use of neutron scattering will continue to increase. However it is likely that such use will only fund a dedicated source when small medium - flux portable sources, probably accelerator-based, become available.

ACKNOWLEDGEMENTS

I would like to thank my colleagues in the execution of the commercial work described, J P Goff, R N Sinclair and C G Windsor, our customers, and the staff at the laboratories at which the measurements were made: ISIS, Risø National Laboratory, LLB Saclay, and ILL Grenoble. The work was partly supported by the Corporate Research Programme of AEA Technology.

REFERENCES
COMPLEMENTARY APPLICATIONS OF SCATTERING BY NEUTRONS AND SYNCHROTRON RADIATION X-RAYS

Yasuhiko FUJII

Institute for Solid State Physics, University of Tokyo
Roppongi, Minato-ku, Tokyo 106, Japan

ABSTRACT

We have demonstrated several topics on condensed matter physics studied with special capabilities of synchrotron radiation x-rays complementary to neutrons.

INTRODUCTION

Since synchrotron radiation x-ray (SRX) became available, some of previously-known disadvantages of x-rays for neutrons have been overcome because of its special capabilities such as finely-collimated intense beams, high resolution, wavelength tunability, perfectly-polarized beams and pulse nature. In this paper, we have demonstrated a wide variety of topics of condensed matter physics studied by our group with a special intention to go beyond neutron capabilities.

TOPICS OF SRX SCATTERING STUDIES

Anomalous Scattering

An Fe/Mn superlattice is an interesting system from a view point of magnetism because of the combination of ferromagnetic and antiferromagnetic materials. To discuss its magnetic properties, it is essentially important to know the composition profile throughout the superlattice, particularly across the interface. Usually x-ray charge scattering has a disadvantage to identify between neighboring atoms in the periodic table as the present case compared with neutron scattering. In fact when an as-grown specimen was checked on a laboratory x-ray source, only first-order peak was faintly observable in a small-angle region. On a synchrotron source, on the other hand, its energy (wavelength) tunability is expected to provide a great enhancement of atomic scattering power due to the anomalous scattering effect near absorption edge. In the present case of the Fe/Mn combination, we can
obtain such an enhancement by a factor of about 10 (100 for intensity) when the incident wavelength is tuned at the Mn K-edge (1.8959Å). Figure 1 displays diffraction profiles of the first-order peak observed on [Fe(15Å)/Mn(50Å)]40 along its layer-stacking direction. This experiment was carried out at BL-4C of the Photon Factory.\textsuperscript{1)} By fixing the wavelength at 1.900Å where we obtained the most enhanced intensity, the longitudinal scanning was extended up to the 8th order peak position as shown in Fig. 2. The Fourier transformation of these intensity data was performed to obtain the composition profile. Figure 3 shows such a profile revealing that the nominally-designed 15Å thick Fe layer is seriously contaminated by the Mn atoms diffused beyond the interface.

Fig. 1
The wavelength dependence of the first-order peak observed on [Fe(15Å)/Mn(50Å)]40.

Fig. 2
Intensity-enhanced diffraction profile observed along the layer-stacking direction in a small-angle region.

Fig. 3
Electron density along the growth direction obtained by Fourier transformation of the observed intensities.
High Momentum Resolution

In a so-called frustrated system having competing interactions, a comensurate-incomensurate(C-IC) phase transition takes place and often a long-period modulated phase (a higher-order commensurate phase) is stabilized. [N(CH3)₄]₂MnCl₄ with space group Pmcn in its normal phase exhibits a phase transition sequence of the modulated structures characterized by the wave number vector of the modulation along the c axis as functions of temperature and pressure. The previously determined phase diagram of this system is shown in Fig.4.²) We started exploration of any higher-order commensurate phases possibly existing in the nominally-designated IC phase in this figure. For this purpose, we used a specially designed Be-cylinder type high-pressure cell with capabilities for controlling pressure ΔP=+0.4MPa and temperature ΔT=+0.05C.³) SRX-ray experiments were carried out on a 4-circle diffractometer at BL-4C of the Photon Factory.⁴,⁵) Figure 5 shows the pressure dependence of the (4,0,ζ) superlattice reflection observed upon compression at a fixed temperature 21.0C. The momentum resolution in this experiment was Δq=1.2x10⁻⁴Å⁻¹ (0.00023c*). One can clearly see a lock-in transition at ζ=3/7 accompanied with remarkable peak-sharpening. By continuing such measurements at fixed temperatures, we succeeded in locating a large number of higher-order commensurate phases in the nominally-designated IC phases as displayed in Fig.6. The present resolution

Fig. 4
Previously obtained phase diagram of [N(CH₃)₄]₂MnCl₄.

Fig. 5
Pressure dependence of the peak profile of the (4,0,ζ) satellite reflection.
Focused Beams for High Pressure Experiments

A large sample volume required for neutron experiment limits the reachable pressure relatively low around 2-3 GPa. On the other hand, the use of a diamond-anvil cell (DAC) and well-collimated synchrotron x-rays now makes it possible to reach several 100 GPa for diffraction experiments from a typically 5-10μm size sample. Figure 7 shows a schematic drawing of our experimental set-up for single-crystal high-pressure experiments with DAC mounted on a conventional 2-axis spectrometer at Photon Factory. A sagitally-focusing double Si(111)

Fig. 6 Higher-order commensurate phases discovered in the nominally-designated 1C phase.

volume $\Delta P \Delta T \Delta q$ achieved in three-parameters space of $P$, $T$ and $q$ is innovatively higher than that in the previous experiment by three orders of magnitude. Figure 6 is reminiscent of the "Devil's Flower" theoretically predicted.6)

Fig. 7 Experimental set-up of the high-pressure SRX diffraction at Photon Factory.

Fig. 8 Diffraction patterns around (200) in the layer-stacking direction of [PbSe (10A)/SnSe(10A)]$_{50}$ superlattice measured on (a) bending-magnet SR and (b) rotating-anode sources. Peak intensity of the strongest reflection is (a) 720 and (b) 1.2 cps.
monochromator incorporated with a pin hole collimator (typically 80μm φ) provides intense monochromatic beams of about 20keV onto a sample. Figure 8 displays how much we improved quality of diffraction data observed on a semiconductor PbSe/SnSe superlattice on a SRX source.  

By using this SRX technique, we studied an interesting layer-by-layer phase transition in an epitaxially-grown PbSe/SnSe superlattice. A bulk of PbSe and SnSe compounds has the cubic B1(Oh5) and orthorhombic B16(D2h16) structures stable at atmospheric pressure, respectively. The B16 lattice can be realized as a denser structure by doubling one of principal <100> axes of the B1 lattice. In fact, PbSe undergoes the B1-to-B16 phase transition at 4.3GPa while the B16 structure is stable in SnSe at lowest up to 34GPa. Hiromi et al. successfully grew epitaxial superlattices of PbSe/SnSe on a NaCl(100) substrate and found four types of structures stabilized systematically depending on the thickness of two layers. Those are [B1/B1], [B1/B16], [distorted B16/B16], and [B16/B16] for the [PbSe/SnSe] layer structure. Samples were removed from the substrate which was dissolved in water and loaded in DAC. Figure 9 displays diffraction patterns around (400) reflection in the layer-stacking direction observed on [PbSe(40A)/SnSe(40A)]25 with the as-grown [B1/B16] structure. When we apply hydrostatic pressure, it contracts as compressibly as bulk and then the PbSe layer undergoes the first order B1-to-B16 transition at 4.3GPa. This fact is directly evidenced in a remarkable change both in diffraction pattern in Fig.9 and in the linear compression curve obtained from the peak

\[
\begin{align*}
\text{Fig. 10} & \quad \text{Linear compression. Closed and open circles represent data points measured with increasing and decreasing pressure, respectively.} \\
\text{Fig. 9} & \quad \text{Pressure dependence of diffraction patterns around (400) along the layer-stacking direction of [PbSe(40A)/SnSe (40A)]25.}
\end{align*}
\]
position as shown in Fig.10. Before we established the present high-pressure SRX technique, we made neutron scattering experiments on the same superlattice loaded in a McWhan-type pressure cell at HFBR of Brookhaven National Laboratory. The highest pressure we reached was 2.3 GPa; therefore, we were not able to find such phase transition previously. The slope of the compression curve in Fig.10 is nearly equal to a bulk of PbSe. Figure 11 summarizes the B1-to-B16 transition pressure (Pc) of the PbSe layer as a function of the number of PbSe atomic planes deposited (m). The transition pressure of a bulk PbSe was measured to be 5.3 GPa by the use of a similarly-deposited thin PbSe film (1000 Å). We have also succeeded in calculating the Pc vs m curve by a phenomenological theory taking the stress effect due to the epitaxial growth into account.

![Graph](image)

**Fig. 11 The B1-to-B16 transition pressure (Pc) versus number of atomic planes of PbSe layer (m). Closed circles represent data points while solid curve shows theoretical calculation expressed by Pc=5.3[1-exp(-0.209(m-5))].**

**Electron Density Distribution**

Solid iodine is known to undergo a gradual insulator-to-metal transition around 16 GPa followed by the molecular dissociation at 21 GPa. Figure 12 shows such structural changes precisely determined by x-ray diffraction. In order to study a process of the metallization, we have recently made an attempt to observe the spacial distribution of 5p valence electrons which are bound in an I2 molecule in its insulating state and are expected to be delocalized in its metallic state. Since a conventional method of photo-electron spectroscopy is not applicable in a high-pressure cell, a precise structure analysis to obtain electron density distribution is only a technique for that purpose. The maximum entropy method (MEM) is employed to analyze

![Diagrams](image)

**Fig. 12 Crystal structures of iodine. Molecular insulator at atmospheric pressure (bottom), molecular metal at 20 GPa (middle) and monatomic metal at 30 GPa (top).**
a limited number of powder diffraction data reliably recorded with Imaging Plate (IP).\textsuperscript{16} Figure 13 shows our preliminary result of electron density distribution observed at 0.6GPa. One can see the bonding electrons between two iodine atoms forming an I\textsubscript{2} molecule as well as an electron cloud stretching towards an adjacent molecule which is probably responsible for electric conduction across a crystal. We are now analyzing further data at higher pressures with a strong hope to detect that these electrons are getting delocalized with increasing pressure and culmination of such a trend results in the metallization and molecular dissociation experi-mentally evidenced.

We demonstrated several topics studied with SRX capabilities which overcome the previously-known disadvantages of x-rays for neutrons. Also intensively studied is SRX magnetic scattering and its resonance scattering. However, neutrons still have a great advantage for identification of low-Z elements and contrast between isotopes(specially H/D) in elastic scattering, lattice/spin dynamics in inelastic scattering, and utilization of polarized beams.

Complementary use of x-ray photons and neutrons are getting more accessible. Such activities are encouraged particularly at major facilities which have both SRX and neutron sources such as PF/KENS (KEK), NSLS/HFBR (Brookhaven), APS/IPNS (Argonne), and ESRF/ILL (Grenoble).

Acknowledgements-
The present works were performed in collaboration mainly with H. Fujihisa, N. Hamaya, Z. Hiroi, T. Matsushita, N. Nakayama, Y. Ohishi, M. Sakata, S. Sasaki, O. Shimomura, S. Shimomura, T. Shinjo and K. Tamemura.

References
4) N. Hamaya, Y. Fujii, S. Shimomura, Y. Kuroiwa, S. Sasaki and
13) Y. Fujii, Y. Ohishi and J. D. Axe, private commun.
NEUTRON REFLECTOMETRY

A. D. Taylor and J. Penfold

ISIS Facility
Rutherford Appleton Laboratory
Chilton, Didcot, Oxon OX11 0QX, UK

The application of specular reflection of neutrons to the study of surfaces and interfaces will be discussed. The theoretical and experimental background to the technique will be presented and a range of recent experimental results from surface chemistry, solid films and surface magnetism given.
NEW TECHNIQUES IN NEUTRON SCATTERING

JOHN B. HAYTER

Solid State Division/FEDC/MS-8218
Oak Ridge National Laboratory
P. O. Box 2009
Oak Ridge, TN 37831-8218, USA

ABSTRACT

New neutron sources being planned, such as the Advanced Neutron Source (ANS) or the European Spallation Source (ESS), will provide an order of magnitude flux increase over what is available today, but neutron scattering will still remain a signal-limited technique. At the same time, the development of new materials, such as polymer and ceramic composites or a variety of complex fluids, will increasingly require neutron-based research. This paper will discuss some of the new techniques which will allow us to make better use of the available neutrons, either through improved instrumentation or through sample manipulation. Discussion will center primarily on unpolarized neutron techniques since polarized neutrons will be the subject of the next paper.

INTRODUCTION

The fluxes of today’s best reactors and spallation sources are within about an order of magnitude of what is achievable with current technology and that limit is going to be approached closely by next generation sources such as the ANS and ESS. Although such a flux increase will offer some new opportunities in itself, neutron scattering experiments will remain signal-limited in most cases, and it will be important to continue the trend started in Europe two decades ago to make the best possible use of the available neutrons. There are four main areas of opportunity. First, to place as many instruments as possible on a given source and to transport the beams to them in an optimal fashion. This has led to extensive use of focusing crystal optics and of neutron guides, but further improvements in beam transport are still possible, especially with supermirrors. Second, the instruments can be improved, either through new methods based on physical ideas such as phase-space transformations or through improvements in hardware such as multidetectors. Third, better theoretical understanding of many complex systems has allowed far more information to be extracted from certain experiments than was thought possible only a decade ago, and this will continue to improve. Finally, clever tricks can be
played with the samples themselves to increase the information content of a given experiment.

In the fields of beam delivery and instrumentation, neutron optics has become a rich field for new development. Techniques being explored today include microbending and microfocussing through capillary guides, divergent beam reflectometry in which the surface is treated analogously to an imaging slit, optical filters for straight neutron guides, and reflectometry studies of interfaces under non-equilibrium conditions such as shear. On pulsed sources, imaging (radiographic) techniques have been extended to thermal imaging by resonant radiography. Tomographic methods developed for medical magnetic resonance imaging (MRI) applications are now being applied to radiography, and interferometer-based phase-contrast microtomography is becoming a possibility as multidetector resolution approaches the few micron level. Phase-space transformations are being considered for a variety of applications. These may simply use focussing or defocussing, or they may trade wavelength bandpass against divergence to obtain a better match between different parts of a spectrometer, for example in backscattering.

The past decade has seen an amazing variety of new fields in neutron science, ranging from experiments related to the astrophysics of the early universe to studies of human biology. Studies of surface and interfacial structure have developed around reflectometry, with liquid surfaces providing an especially rich field, while tunnelling spectroscopy has provided a sensitive probe of the dynamics of molecules on surfaces. New techniques based on theoretical as well as experimental progress have opened up the rich field of complex new materials, which offer a wide variety of practical applications as well as a wealth of basic research topics. Other practical uses are being developed in several engineering fields. Residual strain measurements, for example, are now coming into widespread use at both reactors and pulsed sources.

Sample modification by contrast variation has been limited by chemical difficulties in some important areas such as biochemistry. That situation is now beginning to change as new laboratory techniques are developed. In structural studies, both at small and wide angles, resonance modulation techniques which vary the scattering amplitude of atoms at a given symmetry site in the structure are also starting to be explored again as appropriate instrumentation becomes more readily available. Another sample modification technique coming into widespread use is orientational alignment of structures in complex fluids, which overcomes theoretical difficulties related to correlation of orientation with position; that problem disappears if all structures have the same orientation. In this paper I shall address some of the new techniques which are either just being implemented or are the subject of active research and development. Rather than providing a lengthy catalog of methods, many of which have been discussed in other papers at this conference, I shall concentrate on just a few representative areas which are currently being explored and which may be routine by the time new sources come on line.

NEUTRON OPTICAL FILTERS

Most neutron guide installations have used curved guides, which have the advantage of providing a filtering action against fast neutron and γ background from the source. However, this filtering action also has a disadvantage. To ensure no line-of-sight, the curvature must be such that the guide bends through at least its own width in the length
available. For practical geometries, this leads to characteristic cutoff wavelengths typically around 0.2 - 0.4 nm, so that instruments on cold neutron guides are deprived of shorter wavelengths, and this often restricts the dynamic range of the data which can be taken on the instrument. Further, the neutron optical coating properties determine the guide width once the length and characteristic wavelength have been specified.

Straight guides offer the advantage that the length is decoupled from the width, so that the guide cross-section for a given instrument may be optimized without other restraints. They also transport all available wavelengths (with the usual wavelength dependent solid angle), but whether or not this is an advantage depends on the level of noise transmitted at the same time. Experience at the National Institute of Standards and Technology, which has installed straight guides, confirms theoretical expectations that the $1/r^2$ dilution of noise with distance usually provides adequate signal-to-noise at the distances from the source typical of guide hall instruments (of order 50 m). However, it will almost certainly be desirable to provide even lower noise for certain experiments and some form of filter will be needed. Crystalline filters, such as cooled single crystal silicon or bismuth, may be used as insertion devices to remove fast neutron or $\gamma$ background, but these also cost a non-trivial loss of intensity in the desired wavelength range. We are currently studying the possibility of using a neutron optical deflector as a filter\textsuperscript{2).} This deflector should have the characteristics of a high-pass filter which only transports neutrons above a specified wavelength, but which preserves the beam divergence. Curved neutron guides do not have the latter property; their exit divergence is a function of the guide properties, independent of the incident beam divergence.

![Diagram](image)

**Fig 1. Plan view of an optical filter geometry**

Figure 1 shows a plan view of one possible layout for this type of filter. Conceptually, it is equivalent to one section of a polygonal approximation to a curved guide. The initial Ni guide of width $d$ is followed at an angle $\gamma$ by a length of supermirror guide (SM), after which the Ni guide continues at a further angle $\gamma$. This geometry has the property that a parallel beam is transported with unchanged divergence, unlike the case of a curved guide. (Note that only the horizontal component of momentum is affected, so that the
top and bottom guide coatings may be chosen independently and may, for example, be supermirror throughout.) If \( \gamma \) is taken to be the critical angle for Ni at the shortest wavelength of interest, the supermirror critical angle must be twice that of Ni.

For this geometry, \( L_2 = d / \sin \gamma \), \( L_1 = L_2 - 2d \sin \gamma \), and \( a = d \cos \gamma \). If \( d = 50 \text{ mm} \) and \( \gamma \) corresponds to the Ni critical angle at a characteristic wavelength of 0.2 \( \text{nm} \), \( a = 50 \text{ mm} \), \( L_1 = 14.323 \text{ m} \) and \( L_2 = 14.324 \text{ m} \). The response of this arrangement has been estimated by a simple Monte Carlo simulation in which the divergence of the Ni guide was taken as uniform within the angular range corresponding to each wavelength, with an illumination angular cutoff corresponding to 1 \( \text{nm} \). Figure 2 shows the results. The rectangles are simulation results for the device of fig. 1. The solid line is the response of a curved Ni guide of the same length as the filter and the dashed line is for an equivalent curved guide with a supermirror coating having twice the critical angle of Ni. The results show that the optical filter response is very satisfactory and permits all of the advantages of straight guides to be retained.

![Graph](image)

Fig. 2. Transmission as a function of wavelength for straight and curved optical filters (see text).

**SAMPLE ALIGNMENT AS AN EXPERIMENTAL TOOL**

Many of the fascinating properties of new materials are due to anisotropy of one kind or another, often in a structure which has no long range translational symmetry. Composites prepared via sol-gel methods provide a typical class of examples. The
correlation lengths of interest in these materials are typically in the range nanometers to micrometers, so that small angle neutron scattering (SANS) is often a method of choice. However, if the particles in the structure are correlated (as is usually the case in interesting systems), the scattering theory for such systems has proved highly intractable. The reason for this is that we have no statistical mechanical approach which allows us to compute the probability of a given orientation of one particle with respect to another as a function of distance and the thermal averages cannot be evaluated. However, if all particles have the same orientation, this problem no longer arises.

In many cases of interest, the sample is a colloidal dispersion of anisotropic particles, for example long cylindrical micellar structures in a surfactant or biosurfactant based complex fluid\(^3\),\(^4\),\(^5\). In such systems, application of a hydrodynamic shear is often sufficient to align all of the micelles parallel, allowing fully anisotropic data to be collected and interpreted. There is an interesting variation on this technique when the system is dilute (i.e. the particles do not interact). In this case, a hydrodynamic approximation is available which allows the particle length to be determined from the rate at which the scattering develops anisotropy as a function of the applied shear\(^3\). This means that a SANS measurement on a sheared sample can assess lengths which are too large to measure directly by scattering alone.

![SANS intensity pattern](image_url)

**Fig. 3.** SANS intensity pattern \((Q_{\text{max}} = 3.55 \text{ nm}^{-1})\) for ferrodispersed tobacco rattle virus in 0.5 T applied field

Often there is a need to measure the internal structure of a large molecular structure in solution. Biological structures which may change conformation on crystallization or which cannot be crystallized are a case in point. In these cases the scattering information is very difficult to interpret unless some degree of orientation can be imposed on the system. For systems which are not susceptible to alignment by hydrodynamic shear (because of a small aspect ratio) or by "brute force" magnetic fields (because of insufficient diamagnetic anisotropy) a new method is being tested\(^6\). The macromolecules
of interest are dispersed in a magnetic solvent, such as a water-based ferrofluid, and then a modest magnetic field is applied. Application of a modest magnetic field then aligns the macromolecules due to cross-correlations which develop between the magnetic and non-magnetic particles. Figure 3 shows scattering from the internal helical structure of tobacco rattle virus (TRV), which is difficult to align by any other method.

**RESONANCE MODULATED DIFFRACTION**

Magnetic scattering of neutrons from electron spins has long been one of the most powerful applications of neutron scattering. Scattering from nuclear spins is much less common and generally is only considered insofar as it is a nuisance, causing the strong incoherent scattering background from hydrogenous samples, for example. However, nuclear spin-dependent scattering may be used to great advantage if the nuclear spin polarization in the sample can be manipulated appropriately. Protons, for example, may be turned into "heavy atoms" in diffraction experiments, aiding structure determinations in complicated protonated materials without the need for deuteration and its associated chemical complications. This method, known as resonance modulated diffraction (RMD), required great experimental complexity at the time of its first application\(^7\) and was generally considered too difficult for general use. Advances in high-field, low temperature technology now permit its application fairly easily and there is renewed interest in the method.

Consider a sample in which the atom at position \( R_\nu \) has nuclear spin \( I_\nu \). The coherent (COH) and incoherent (INC) scattering cross-sections for this system at momentum transfer \( \mathbf{Q} \) are

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_{COH} = \left| \sum_\nu \frac{1}{(2I_\nu+1)} \left[ ((I_\nu+1)a_\nu^++I_\nu a_\nu^-)\pm I_\nu(a_\nu^+-a_\nu^-)p_\nu \right] \exp(i \mathbf{Q} \cdot \mathbf{R}_\nu) \right|^2
\]  

(1)

and

\[
\left( \frac{\partial \sigma}{\partial \Omega} \right)_{INC} = \sum_\nu \frac{I_\nu(I_\nu+1)}{(2I_\nu+1)^2} (a_\nu^+ - a_\nu^-)^2 (1-\gamma_\nu^2 p_\nu - \gamma_\nu^2 p_\nu^2)
\]  

(2)

where \( p_\nu = I_\nu/I_\nu \) is the local nuclear polarization, \( a_\nu^+ \) and \( a_\nu^- \) are the singlet and triplet scattering amplitudes, and the sign in eqn (1) is chosen according to the incident neutron polarization. When the nuclear polarization is zero (the usual case) these equations take the usual familiar forms.

The cross-sections (1) and (2) have interesting properties. First, when \( p = 1 \), the spin-incoherent scattering from the sample disappears completely; greatly improving experimental signal-to-noise. (Any isotropic incoherence will still be present, but for hydrogenous samples the noise is dominated by proton incoherence.) For an unpolarized beam the effects of polarization average to zero in eqn (1), but for a polarized beam the coherent cross-section may be greatly increased or decreased, depending on the relative directions of the neutron and nuclear polarizations. In particular, when the latter are
opposed, the coherent cross-section for a given polarization site becomes zero when

$$|p| = \frac{(I+1)a^+ + Ia^-}{I(a^+ - a^-)}$$

which for protons \((I = \frac{1}{2})\) is 0.27. Thus scattering from atoms at a particular symmetry site may be removed from the cross-section (1) for a polarized neutron beam if the local sample polarization can be appropriately controlled.

![Graph](image)

**Fig. 4.** Spin-dependent Bragg scattering from a hydrogenous sample with polarized nuclear spins

Figure 4 shows the large enhancement in scattering which can be achieved for one neutron spin state, and the suppression of scattering for the other spin-state, for Bragg scattering from a heavily hydrated crystal. In this experiment the nuclei were polarized by double resonance techniques using 69 GHz (4 mm microwave) ESR and 78 MHz NMR at 2.3 T and 1.5 K. When the radiofrequency pumping is removed, the scattering decays to the mean (unpolarized) value with the nuclear spin-lattice relaxation time constant (25 minutes in this case). Double resonance techniques have certain advantages but they are relatively complicated. Fortunately, commercial cryomagnets are now available which allow the use of simple thermal equilibrium in a field to polarize the nuclei.

The major interest of the technique lies not in the ability to enhance the signal and suppress the incoherent scattering, but in the possibilities it offers for the performing the equivalent of selective deuteration, site by site, simply by applying a radiofrequency field. Once the sample is polarized, the scattering from the atoms in a given symmetry class may be selectively "darkened" by applying the appropriate NMR frequency to depolarize that symmetry site. This may be done on a site-by-site basis, so that a series of Bragg intensities may be collected in which the scattering from different sets of atoms has been systematically altered in the unit cell. Figure 5 shows the effect on the system of fig. 4. The radiofrequency pumping is left on while the NMR frequency is scanned, with constant "spin up" neutron polarization throughout the scan. The sharp dip in intensity at the resonant frequency is clearly evident.
ACKNOWLEDGEMENTS

This work was supported by the Division of Materials, U.S. Department of Energy. Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

REFERENCES

Applications of Polarized Neutrons

F. Mezei

BENSC, Hahn-Meitner-Institut, Pf. 390128, 14091 Berlin

Abstract

The additional spin degree of freedom of the neutron can be made use
of in neutron scattering work in two fundamental ways: (a) directly for
the identification of magnetic scattering effects and (b) indirectly as a
spectroscopic tool for modulating and analysing beams. Although strong
magnetic scattering contributions can often be studied by unpolarized neu-
trons, a fully unambiguous separation of nuclear and magnetic phenomena
can only be achieved by the additional information provided by polarized
neutrons, especially if one of the two kinds of contributions is weak com-
pared to the other. In the most general case a sample with both magnetic
and nuclear features can be characterized by as many as 16 independent
dynamic correlation functions instead of the single well known \( S(q,\omega) \) for
non-magnetic nuclear scattering only. Polarization analysis in principle al-
 lows one to determine all these 16 functions. The indirect applications of
polarized neutrons are also steadily gaining importance. The most widely
used method of this kind, the application of Larmor precessions for high
resolution energy analysis in Neutron Spin Echo spectroscopy opened up a
whole new domain in inelastic neutron scattering which was not accessible
to any other spectroscopic method with or without neutrons before.

Introduction

The utilization of spin polarized neutron beams in neutron scattering work was
started in 1951 by C.G. Shull's diffraction study of magnetite [1], although the theoreti-
cal foundations had been laid much earlier, shortly after the discovery of the neutron [2].
Since then polarized neutrons have become a traditional accessory of neutron diffraction
investigation of primarily ferromagnetic and ferrimagnetic samples, which can be fully
magnetized. Inelastic magnetic processes, such as magnons, could also be singled out
by polarized neutrons in the same class of samples, although this has really been done
much less often. I shall not include these classical applications in the present survey,
but rather concentrate on a few selected, more recently introduced approaches, which
appear to make part of emerging trends of increasing importance in the future. This
rather arbitrarily chosen list of recent highlights includes

1.) general vectorial (or 3 dimensional) polarization analysis studies of magnetic struc-
tures
2.) determination of generalized and local magnetic susceptibilities in paramagnets
3.) generalized Neutron Spin Echo (NSE) spectroscopy for the investigation of phonon lifetimes.

To start with, a short reminder will be presented in order to review the current situation with polarizer and analyser systems from the point of view of availability and performance.

**POLARIZERS AND ANALYSERS: STATE OF THE ART**

The extra information obtainable by the observation of the dependence of a neutron scattering cross section on the neutron beam polarization (called "scattering of polarized neutrons") or by determination of the scattered beam polarization as a function of the incoming beam polarization (called "polarization analysis") is usually rather dearly paid for by a loss in beam intensity. This particularly handicaps polarization analysis, where both polarizer and analyser are needed. The undue intensity loss is primarily related to the limited beam divergence accepted by polarizers (e.g. insufficient mosaic for crystals or small critical angle for mirrors). Supermirrors with a critical angle of about 0.2 deg per Å wavelength provide a satisfactory solution for $\lambda \gtrsim 3\text{Å}$, and this wavelength limit might be improved in the future, if higher critical angle mirrors become available in sufficient quantities. In particular, supermirror polarizers can handle the full beam divergence contained in a standard Ni coated guide with losses smaller than about 30% (beyond the 1/2 spin population factor). This is exemplified by the beam splitter polarizer system, which is presently set up at one of the neutron guides at BENSC in Berlin [3]. Here the neutrons are selected according to their spin state into two beams serving two instruments. Both beams offer a broad wavelength band with uniformly high polarization and transmission coefficients (Fig. 1).

The situation is less satisfactory with analysers, although Soller type supermirror systems can in principle be put together into analysers with large solid angle acceptance. The problem is the quantity of supermirrors required: in order to cover 1 m$^2$ of detector area an analyser system for $\lambda \gtrsim 3\text{Å}$ will consist of some 60 – 200 m$^2$ of supermirrors depending on the lay-out, i.e. some 3 to 10 years production of a $\$ 1$ Mio vacuum deposition machine. The largest solid angle analyser set in existence today is the one on D7 spectrometer [4] at ILL covering about 0.1 m$^2$ total detector surface (32 detectors) using some 25 m$^2$ of supermirrors, the deposition of which took over 4 full years for W. Graf working with O. Schärpf. The largest area single analyser element is the one used on the NSE spectrometer IN 11 with an area of about $9 \times 9 \text{cm}^2$ containing 0.6 m$^2$ of supermirrors [5]. On each of these instruments the counting rate in each detector in a polarization analysis experiment is at least 2 times superior at a wavelength of 5 Å compared to the best existing thermal triple axis spectrometers at the peak of the polarized flux. This means for D7 2 orders of magnitude higher data rates, however without energy analysis and with the additional limitation that due to the use of cold neutrons only relatively slow magnetic fluctuations can be studied efficiently (up to few meV).

For shorter wavelengths thermal neutrons the hope of producing graphite quality Heusler crystal polarizers has still not been fulfilled beyond a few lucky strikes of insufficient number. The relatively large d spacing, 3.35 Å also is a drawback for the resolution both in diffraction and in inelastic spectroscopy. A promising real breakthrough is seen now in developing non-monochromatizing polarized $^3\text{He}$ gas filters, which will work in a broad wavelength range including $\lambda \leq 1\text{Å}$. This kind of filters are being developed for
nuclear physics experiments with considerable effort and although there are encouraging results, it is not at all clear by now if the cell size and stability required for sensible neutron experiments will become attainable any soon at affordable costs.

FUNDAMENTALS

Conventional polarization analysis as introduced decades ago [6] is only concerned with one component of the neutron spin polarization vector, say \( P_z \), where \( z \) is parallel to the field direction on the sample. Thus the polarization can be defined in terms of the occupation numbers \( n_\uparrow \) and \( n_\downarrow \)

\[
P_z = n_\uparrow - n_\downarrow
\]  
(1)

where "up" and "down" refer to the \( z \) direction and \( n_\uparrow + n_\downarrow = 1 \). In this description the scattering process can be fully accounted for by 4 partial cross sections \( t_{ij} \), which are in fact the transition probabilities between neutron spin states \( i \) to \( j \) (\( i,j = \uparrow, \downarrow \)), and the scattered beam polarization \( P'_z = n'_\uparrow - n'_\downarrow \) is given by the matrix equation

\[
\begin{pmatrix}
  n'_\uparrow \\
  n'_\downarrow
\end{pmatrix} =
\begin{pmatrix}
  t_{\uparrow\uparrow} & t_{\uparrow\downarrow} \\
  t_{\downarrow\uparrow} & t_{\downarrow\downarrow}
\end{pmatrix}
\begin{pmatrix}
  n_\uparrow \\
  n_\downarrow
\end{pmatrix}
\]  
(2)

Thus, this scalar approach can provide 4 independent parameters about the sample, which are actually functions of the momentum and energy transfer variables \( (q, \omega) \). This is a tremendously reduced picture, since the neutron spin, and therefore the neutron polarization in general is a 3 dimensional vector, and the interaction between neutron and sample is a tensor. In Ref. [7] it has been recapitulated in detail that the \( S = \frac{1}{2} \) character of the neutron spin leads to a maximum of 16 cross sections, which are independent of each other in the spin variable and can theoretically all be determined by the vector polarization analysis methods. It is interesting to note that a generally overlooked piece of experimental work at St. Petersburg (Leningrad then) demonstrated
the feasibility of vector polarization analysis [8] before the scalar variant was described at Oak Ridge. The most widely used example of vector polarization work yet is NSE spectroscopy [9].

Just to summarize (for details see Ref. [7]), the wavenumber dependent Hamiltonian potential for the neutron scattering process is:

\[ V = -\vec{\mu}B(\vec{q}) + \sum_i e^{i\vec{q}\cdot\vec{r}_i}(b_i + a_i\vec{r}_i) \]  \tag{3}

where \( \vec{\mu} = 1.913\mu_N\sigma \) is the neutron spin, and the sum goes over the nuclei in the sample. Following Maxwell’s equations the Fourier transform of the magnetic field \( \vec{B} \) can be expressed by the magnetization \( \vec{M} \):

\[ \vec{B}(\vec{q}) = \vec{M}(\vec{q}) - [\vec{q}\vec{M}(\vec{q})]/q^2 \]  \tag{4}

Eq.(3) leads to transition probabilities (cross sections) of the most general form

\[ |<\lambda',\chi' | b(\vec{q}) + \bar{a}(\vec{q})\sigma | \lambda,\chi>|^2 \]  \tag{5}

where \( \lambda, \chi \) are the initial states of the sample and the neutron spin, respectively, and \( \lambda', \chi' \) are the final states. For any transition \( \lambda \rightarrow \lambda' \) this scattering matrix element depends on 4 complex numbers: \( <\lambda' | b(\vec{q}) | \lambda> \) and \( <\lambda' | \bar{a}(\vec{q}) | \lambda> \), i.e. 7 parameters with one phase being fixed arbitrarily. In an ideal sample, Bragg scattering processes are good conceptional examples for single state transitions: \( \lambda \) and \( \lambda' \) can be taken equal to an effective “ground” state \( \lambda_0 \). Thus, in magnetic crystallography one has to be able to determine 7 independent parameters by polarization analysis. Thus the scalar approach is insufficient. This does not imply that 7 spin parameters per Bragg reflection are sufficient to determine the structure, but that they contain all information visible to the \( S = \frac{1}{2} \) neutron.

Realistic samples are most often magnetically not monodomain and the manifold of thermally excited states are also to be taken into account in the determination of the Debye-Waller factors and diffuse scattering processes. Consequently, we cannot only consider a single transition matrix element \( \lambda \rightarrow \lambda' \) in eq.(5) but have to average over the initial states \( \lambda \) and the sum over the final states \( \lambda' \). This process leads to 16 independent correlation functions: \( <b^\ast b>, <a^\ast_\alpha a_\alpha>, Re a^\ast_\alpha a_\alpha, Im a^\ast_\alpha a_\alpha, Re a^\ast_\alpha a_\beta, Im a^\ast_\alpha a_\beta \), where \( \alpha \neq \beta \). Let us recall that all of these correlation functions are functions of \( \vec{q} \) and \( \omega \).

Finally it remains to recall that these 16 independent correlation functions can really be experimentally determined. The polarization dependence of the scattering cross section can most generally be written in the form of

\[ \frac{d^2\sigma}{d\Omega d\omega} \propto A(\vec{q},\omega) + \vec{B}(\vec{q},\omega)\vec{P} \]  \tag{6}

where \( A \) and \( \vec{B} \) are a real scalar and a real vector, respectively. In the same manner the scattered beam polarization is obtained as

\[ \vec{P}_f \frac{d^2\sigma}{d\Omega d\omega} \propto \vec{C}(\vec{q},\omega) + \vec{T}(\vec{q},\omega)\vec{P} \]  \tag{7}

where \( \vec{C} \) is a real vector and \( \vec{T} \) a real tensor. These linear equations would be a first approximation for classical \( (S \rightarrow \infty) \) spins, but for \( S = \frac{1}{2} \) higher order terms do not exist.
A, \vec{B}, \vec{C} and \mathcal{T} are the measurable quantities and they represent exactly 16 independent components. It can be shown that the equations expressing the above 16 correlation functions in terms of these 16 measurable parameters can be uniquely solved [7]. Thus vector polarization analysis makes accessible all information on the scattering potential the neutron can see at all.

**VECTOR POLARIZATION ANALYSIS**

After the pioneering work of the St. Petersburg group and some further partial results and proposals a new set-up has been developed by F. Tasset and co-workers at ILL [10], which allows to perform the vectorial polarization measurements as defined by eqs.(6) and (7) for the first time with sufficient precession at any scattering angle. The apparatus dubbed CRYOPAD is an extremely elaborate set of guidefields, precession and flipper coils and superconducting shields (Fig. 2). A first set of beautiful experiments could be completed before the shut down of ILL, e.g. correction of earlier proposed magnetic crystal structures by revealing the complex non-collinear nature of the magnetic order [11].

**GENERALIZED AND LOCAL SUSCEPTIBILITIES IN PARAMAGNETS**

In order to understand the magnetic susceptibility of paramagnets with strong interactions (e.g. strongly correlated electron systems) the temperature dependence of the susceptibility provides too little clue, actually in form of deviations from the Curie law \( \chi(T) \propto \frac{1}{T} \). Such deviations are either due to a temperature dependence of the localized magnetic moments (e.g. Kondo effect) or to correlations between neighbouring magnetic moments. These correlations are expressed by the generalized susceptibilities \( \chi^{\alpha \beta}(\vec{q}) \), which describe the \( \beta \) component of the response induced by the \( \alpha \) component of a staggered field. For systems with reasonable symmetry properties only \( \alpha = \beta \) contributions are not negligible, and the relation between susceptibility and neutron scattering cross section due to the \( \alpha \) component of the paramagnetically fluctuating moments reads [12]

\[
\chi^{\alpha}(\vec{q}) \propto \frac{1}{kT} \left( \frac{d\sigma}{d\Omega} \right)^{\alpha}_{PM}
\]

This equation holds in the quasielastic approximation only, i.e. if the neutron energy change is small compared to both the initial neutron energy and to \( kT \). This is also a practical condition for directly determining the cross section \( d\sigma(\vec{q})/d\Omega \) by collecting neutrons without energy analysis like in ordinary two axis diffraction, since the energy integration of \( d^2\sigma(q,\omega)/d\Omega d\omega \) usually is a hopeless task with the low intensities involved. One of the main reasons why higher energy polarized neutrons would be so valuable, is just to achieve safer energy integration of the scattering response.

The problem of determining \( \chi^{\alpha}(\vec{q}) \) via eq.(8) is the high background of nuclear (incoherent, multiple-Bragg, phonon and multiphonon) scattering. Polarization analysis offers a straightforward solution in macroscopically isotropic samples: \( \chi = \chi^{\alpha}, \alpha = x, y, z \). The isotropic magnetic behaviour will result in a characteristically anisotropic polarization behaviour with respect to \( \vec{q} \) due to the second term in eq.(4), while the other
Fig. 3. Signature of ferromagnetic shortrange order in the generalized susceptibility of $V_5O_9$ [13].

Fig. 4. Distribution of local magnetization induced in a $Y-Ba-Cu-O$ sample by a 4.6 T field [16].

contribution to the $\bar{a}(\vec{q})$ vectorial term in (5), the nuclear spin interaction $\vec{I}_i\vec{\sigma}$ in eq.(3) remains isotropic. The result is the famous Halpern-Johnson equation $\vec{P}' = -\vec{q}(\vec{P}\vec{q})/q^2$ for the paramagnetic response, and $\vec{P}' = -\vec{P}/3$ for the nuclear spin response. The scalar term in (5) leads to $\vec{P}' = \vec{P}$. To sort out a sum of these three types of behaviour it is sufficient to determine the 3 diagonal elements of the tensor $T$ of eq.(7) in a coordinate system adequately chosen in view of the possible directions of $\vec{q}$ [9].

A recent example [13] is shown in Fig. 3. The generalized susceptibility $\chi(q)$ has been determined in the metallic ($T>170 \, K$) and insulating phases of a $V_5O_9$ powder sample, using D7 and IN11 spectrometers at ILL. The macroscopic susceptibility $\chi(q=0)$ shows a jump at the metal–insulator transition from an expected $2.1\mu_B/\text{per } V \, \text{atom}$ Curie behaviour in the metallic phase to some 3 times smaller value. Up to now this has been interpreted as an onset of antiferromagnetic nearest neighbour correlations in a Mott type insulator phase. The neutron results reveal that quite to the contrary, the atomic moments in the metallic phase are rather small ($\sim 0.6\mu_B$) and the higher susceptibility is due to ferromagnetic correlations. Thus we rather have to do with an itinerant, strongly correlated electron metal and not with quasi-free atomic moments.

In strongly temperature dependent phenomena, e.g. critical scattering above a phase transition, the requirement of isotropic sample behaviour can be dropped under the assumption that the nuclear background is temperature independent so that the identification of the nuclear and magnetic contributions can be performed by the above approach at a high enough temperature, where the sample can be considered isotropic. Then, above a now well known background, the temperature dependent anisotropy can be observed within the plane perpendicular to $\vec{q}$, the magnetization component parallel to $\vec{q}$ being cancelled in eq.(4). In a single crystal near to a Bragg peak full anisotropy studies are also possible since here $\chi^\alpha$ will depend on the reduced variable $\vec{q}_r = \vec{q} - \vec{\tau}_{hkl}$, (which can e.g. be perpendicular to $\vec{q}'$), while the total momentum transfer $\vec{q}$ applies to eq.(4). This way it was possible to determine the predicted dipolar anisotropy of the
critical fluctuations at the Curie point of isotropic ferromagnets [14], i.e. to show that only $\chi_\perp(q)$ diverges critically, while $\chi_\parallel(q)$ tends to a constant as $q \to 0$ and $T \to T_c$. Here $\perp$ and $\parallel$ stand for parallel and perpendicular to $q$. (This experiment also only implies the determination of diagonal elements of the tensor $T$.) More recently, the more difficult task of determining the dipolar anisotropy of the inelastic critical scattering $d^2\sigma/d\Omega d\omega$ has also been accomplished by the same polarization analysis trick [15].

![Graph](image)

**Fig. 5.** Phonon linewidth due to spontaneous phonon decay in superfluid $^4He$ at $T \to 0$ [18].

The determination of the local susceptibilities, on the other hand, is a generalization of polarized neutron crystallography, making use of improved efficiency of the instruments. A high magnetic field is applied to paramagnetic samples introducing a polarization corresponding to the $\chi(q=0)$ susceptibility. The distribution of this induced magnetic density is then determined in the form of magnetization maps by single crystal diffraction methods. The results allow to identify the contribution of individual atomic sites to the total magnetization with the impressive sensitivity of $< 0.001 \mu_B/atom$. Fig. 4 shows an example obtained in Y-Ba-Cu-O [16]. The higher polarizability of the Cu atoms on the chain sites compared to the antiferromagnetically coupled Cu in the planes and the contribution of O sites are the marked features put to evidence.

**GENERALIZED NEUTRON SPIN ECHO SPECTROSCOPY**

In common applications of Neutron Spin Echo (NSE) spectroscopy quasielastic scattering processes are investigated with a high resolution of some 0.01 $\mu$eV (sensitivity even higher) corresponding to characteristic times of up to $10^{-7}$ sec. This has opened up a new field of applications of neutron scattering spectroscopy in the study of slow processes. An similarly important extension of the capabilities of neutron methods can be expected from the generalization of NSE for the studies of elementary excitations first proposed in 1977 and demonstrated in 1979 [9, 17]. The method, however, has only been applied in a very small number of real experiments on superfluid $^4He$, due to technical difficulties and to the small capacity available for tackling such difficulties in the physics community busily producing publications on a faster pace than technical development work is likely to permit. The latest example of these few results is shown
in Fig. 5 [18]. The lifetime of phonons in superfluid $^4\text{He}$ at $T<1\text{K}$ is dominated by the anharmonic decay of one phonon into two others. At low pressures these processes are kinematically only allowed for $q \leq 0.43\ \text{Å}^{-1}$, due to the particular shape of the dispersion relation. The energy resolution in this example is better than $10^{-3}$, i.e. nearly two orders of magnitude better than the some 50 $\mu\text{eV}$ available by conventional spectroscopy. Because such a resolution improvement would imply an intensity loss by a factor of some $10^4$ or more using conventional methods, the focussing feature of the NSE approach offers the only possible way to avoid this kind of intensity penalty.

The technical difficulty of generalizing NSE for the study of elementary excitations (beyond obtaining a reasonable flux in polarization analysis) resides in the necessity to tune the shape of the precession fields too [9, 17]. This technical problem can be solved much easier by the recently developed Zero Field NSE trick [19] (which is based on the use of r.f. flippers instead of the d.c. ones in ordinary NSE) and it is to be expected that the results of the work in progress in collaboration of TU Munich and BENS on the implementation of ZF-NSE on a triple axis instrument will make this kind of studies more generally accessible and feasible.

REFERENCES

Panel Discussion

Future Research with Neutrons

—from JRR-3M to Next Generation Neutron Sources—

Chairman: Y. Yamada (Osaka Univ. Prof. Emeritus)

Chairman: Good afternoon, ladies and gentlemen. Let us now start the last session. This session is dedicated for a Panel Discussion under the title of "Future Research with Neutrons: from JRR-3M to Next Generation Neutron Sources", which is, as you see, a rather broad subject.

The discussion will be made mainly by these ten panelists. Perhaps most of you are already familiar with the faces of these panelists, but just for formality let me first introduce the names and their affiliation. To begin with, first from my left-hand side,

Dr. Bruno Dornier from Institut Laue-Langevin,
Professor Yasuo Endoh from Faculty of Science, Tohoku University,
Dr. John Hayter from Oak Ridge National Laboratory,
Dr. Eiji Shirai from JAERI, and
Dr. Satoru Funahashi from JAERI.

On the right-hand side,

Dr. Gerard Lander from European Institute for Transuranium Elements,
Professor Yasuhiko Fujii from the Institute for Solid State Physics, the University of Tokyo.
Dr. John Carpenter from Argonne National Laboratory,
Professor Noboru Watanabe from Institute for High Energy Physics,
Dr. Motoharu Mizumoto from JAERI.

And myself,
Sada Yamada, ex-Professor of Institute for Solid State Physics, the University of Tokyo.

Before going into detailed discussions by each panelist, just for your convenience, let me give you the scope of this panel. The discussions are broadly divided into two categories. The first category is, so to speak, hardware-like aspect. That is, the neutron source facilities. This is certainly the central issue of this panel as is explicit in the subtitle. The other is, on the contrary, the software-like aspects, such as effective utilization of these neutron sources, international collaboration, the direction of future neutron scattering research, etc. The first subject may be further divided into two subcategories, namely steady source and pulsed source. We will start from the topics on steady source, then move on to the pulsed source and finally get into the discussions of software aspects.

After the presentation of one of these three topics, I will stop the discussion and give some time for free discussions on that topic. Comments from the audiences as well as discussions between the panelists are very welcome. So, please feel free to give some comments from your seat. Each panelist, please observe the counter which is counting down your allocated time so that you do not go over the limit.

Part 1

Chairman: Okay, now let’s start from the first speaker. The first speaker is Dr. John Hayter from Oak Ridge National Laboratory.

Hayter: Thank you. I talk this morning a little about what you might do, given a new source or even an existing one. What I want to spend ten minutes or so on now is the fact that the source is not enough. To have a source, even well instrumented, is of no use if it’s difficult to use or it has no other form of support.

Let me illustrate that with the design thoughts that have gone into the design of the Advanced Neutron Source. I will give you a brief look at what scientific facilities are planned.

First of all, the unperturbed thermal flux is about $7.5 \times 10^{15} \text{n cm}^{-2} \text{s}^{-1}$. The reflector tank is 3 m in diameter and at almost every point in the heavy water the flux is higher than the ILL peak flux. There are many provisions for neutron scattering. Despite the fact that we believe most high
energy work will be done on spallation sources there is still some need for hot beams. There are thermal beams, cold sources with straight guides, and slant beams to an upstairs beams to transport very cold neutrons for optics work.

The ANS also has to replace the High Flux Isotope Reactor which will be shut down when the ANS starts. So we also have to have capabilities for isotope production and in particular, we will be essentially the only supplier in the world of $^{252}$Cf for medical use and radiography, and Einsteinium which is the starting point for heavy ion bombardment to try and make the super heavy elements. We must also support research in nuclear physics, materials irradiation, and extensive capabilities for activation analysis.

Now, there is one point I want to make here and that is the flux here is only five times greater than Grenoble. Physicists are used to dealing in orders of magnitude. We've already talked here about 10 or 12 orders of magnitude in energy, 6 in momentum and so on. In engineering an order of magnitude is unbelievable. It is difficult to get. To put that into perspective, Lindbergh flew the Atlantic in 32 hours. The Concord is not 10 times faster. It is very difficult in engineering to get factors of 10. Nevertheless, some of you will get the feeling that the Concord is better than 10 of Lindbergh's aircraft. And one of the reasons that it is better is that there are more seats on the aircraft and that's where we come to a lot of beams and a lot of instruments. That's the important thing. The equivalent in the spallation source is multiple targets.

So it's not just the question of a good source, you've got to get the neutrons to samples and lots of samples. To try to get a realistic measure of the gain factor, I have integrated beam areas times source flux for each beam at major facilities. You see, first of all, for hot neutrons we are not planning to do much better than the ILL. We are not particularly concerned in trying to make great leaps in hot flux. The spallation sources will do that. For thermal flux we will do significantly better than just the factor of 5 because we are going to have different shape beams and bigger beams. For cold neutrons we will be more than 20 times Grenoble in terms of neutrons delivered to the samples. That is because we have two cold sources and we have more than twice as many guides. All the zero's here (cold neutrons) from North America tell you why you need the ANS.

Now, in trying to design the world's best reactor engineers, of course, will focus on the reactor which has a very efficient core with about 18 kgs of enriched uranium operating at 330 MW. There is a heavy water reflector tank, about 3 m in diameter, with many guides looking at each cold source and then lots of other thermal beams. A big attempt will be made to make a good signal to noise ratio, which is important. Any time you can get the noise down, it's often equivalent of a reflection increase. So all the beams, for example, are tangential.

But when it is all said and done, who cares? If you are doing research, the source is a black box. I don't care what produces the neutron counts as long as there is plenty of them, and if I could do it with a kilogram of Californium I might do it that way. It's the infrastructure that says whether you have a good research lab or not. So when you have lots of instruments we need lots of room for them, and we need lots of support area for labs: chemistry labs, biochemical labs and so on. You also need room for expansion, which we have provided here. There will be a large guide hall, with two instruments per guide, one of them mid-position and one end-position on each guide so there is room for expansion there.

Next to the guide hall is an experimental support building with several floors of labs, workshops and so on. And then in close proximity is the office building with conference areas. The distance from here to the end of the guide hall is somewhat over 100 m. So distance from office to instrument matters. All of that is no good if you cannot get into the place. If you try to enter a reactor with the faint glimmering of a new scientific idea and someone points an M-16 at you with his finger on the trigger, by the time you leave, whatever scientific idea you had is gone. That is a lousy way to do business. And the reason you have that situation is because there is no much more concern with security, anti-terrorism and so on, that anyone conceived when these old existing facilities were designed. If you think of it from the beginning, then you can do a great deal to improve security.

So at the ANS, this is the experimental area with the beam room, the guide hall, experimental support, laboratories, workshops, office space, conference rooms and so on. These are reactor operations areas. And that is a Berlin Wall separating the experimental and operational areas. It is not administrative control, it is 6 or 8 or 10 feet of concrete through the entire structure in three dimensions. They can keep the nuclear side totally secure, and the experimental side is totally open. And that's an extremely important feature. You will be able to drive in with the same ease or perhaps even slightly more ease than you can do at the ILL. And that extends to the second floor, half of the second floor is also an experimental area. We have a lot of visits by school children and others at Oak
Ridge, something between 30,000 to 40,000 a year from high schools. You don't want those people tramping through your experiments. So we have a visitor's gallery here, again with direct access but with absolute security that they cannot get to the operations area.

This is an architect's model which tries to embody all these principles where a visitor arrives at this end and comes into the reception area or office space with free access. You would need a pass to get into the experimental areas, and you cannot get to the other side (operations area) at all if you are an average user.

As I said this morning, we are in the President's budget for construction starting in '94 and in 2001, this will be the operating Advanced Neutron Source facility to which you are all invited to do experiments.

Thank you, Mr. Chairman. You see I've saved you some time.

CHAIRMAN: Thank you very much for saving time. Let's move on to the other two speakers who are going to talk on a similar topic. Dr. Shirai, please.

SHIRAI: Thank you, Mr. Chairman. I am working in the research reactor field. I am in charge of research reactor operation and utilization in JAERI, so I am managing the JRR-2, JRR-3M and JRR-4 in JAERI.

From the research reactor side, I would like to present some comments. At first, you already know that we finished the construction of the upgrading program of JRR-3. This shows the requirements for the upgrading program of JRR-3. We have the JMTR for irradiation use. So, we set for the JRR-3M that the target of its utilization was neutron beam experiments. For the performance, it is very difficult to get a big research reactor in Japan, so we set for the thermal neutron flux, which was higher than JRR-2 the present research reactor in JAERI. And we would like to have high quality neutron beams including the cold neutron source and neutron guide tubes in JRR-3M. We also installed the high performance irradiation facilities. In some cases, the activation analysis is very important for using the research reactor, so we set the activation analysis system.

At the present time, we got a good result for upgrading program in JRR-3. We think these requirements were good selection for the research reactor modification.

Next, recently we investigated the needs for the research reactor utilization. Only a short explanation but on the result of the investigation. One of the objects of the utilization of research reactors is neutron activation analysis. The radio isotope production is already established in research reactor utilization. But the other one of the utilization is neutron scattering experiments. These are the two main uses for the research reactors, we think.

This shows the purpose of the capsule irradiation in JAERI. In 1991 fiscal year, we had many irradiation capsules. About three quarters were used for activation analysis. So nowadays it seems that the research reactors are mainly used for activation analysis.

I would like to introduce another data; this shows number of the irradiation capsules in these reactors in JAERI for the past ten years. The yearly total number of the capsules irradiated is almost the same, there are no change. But in the fiscal year 1991 we started the utilization of new JRR-3M. Now it is like this. So in the future the number of irradiation capsules in JRR-3M will be increased.

I would like to introduce another data. This is the data for beam experiments in JAERI. Several years ago, we only had JRR-2 and old JRR-3, but at that time, the machine time for the beam experiments was around this level. These are the instrument days, the days for the utilization of the beam experiments. But after the completion of JRR-3M, like this, the capacity for beam experiments is increased, but the demands of the use of the beam experiments are like this, bigger than that.

I would like to summarize that the research reactor has a lot of merits for the future neutron source. Reactors have large utilization volume, large quantity of the neutrons and we can get low energy neutrons especially cold neutrons and ultra cold neutrons for utilization.

In the future, the ultra high neutron-flux reactor would be a very valuable steady state neutron source. Therefore, the Advanced Neutron Source, ANS project, Dr. Hayter introduced to us, which is under way the conceptual design stage in the ORNL is a very interesting project for us. It is my personal opinion but we would like to cooperate for the completion of this project.

Also, thinking about the life of the new JRR-3M and change of needs for reactors, ten or fifteen years later, we would like to construct an advanced research reactor in JAERI. It will be a central facility for neutron utilization research in Japan. Good and convenient facilities can get many users in many fields. So we would like to continue research and developing works for a new research reactor and the advanced utilization equipment. Thank you.
CHAIRMAN: Thank you very much. Dr. Funahashi will continue or supplement Dr. Shirai’s discussions.

FUNAHASHI: To begin with, let me show you this figure to discuss "from JRR-3M to Future Neutron Sources". The number of neutron scattering machines at JAERI is shown as a function of the year. In 90 at the completion of the JRR-3M, it increased up to about 25 or a little more than that, including the utilization of the JRR-2. This number includes both the machines of JAERI and also those of universities. Classified numbers are not shown here but the proportion of these machines are shown: triple-axis, small-angle scattering, standard diffractometers and another kind of diffractometers are the major part of them.

For our JAERI group, we have eight machines among them. Two of them are not scattering instruments but the rest six are scattering machines. All of them are showing very good performances. I believe their performances are of the first class in the world but all of them are conventional from the view point of the type of machines. They are conventional because we have constructed them in the first step plan of the utilization of JRR-3M.

Now after three years since their completion, we are going to develop new instruments. One is a machine for structural analysis of biological materials. Another is a machine to develop devices to make good use of cold neutrons. The latter will be built on the cold guide.

But for the biology machine, we have a little problem of neutron beam. For the moment we are thinking of sharing the beam of the high resolution powder diffractometer HRPD, because we have been thinking of having a four-circle diffractometer in mind from the beginning of the construction of HRPD. So if the biology doesn't need much big beam, if it will be a small beam for single crystals of usual size, that will not make a big problem. But Dr. Niimura, who is thinking of building that machine there, is planning to put a big monochromator in the beam of HRPD and to focus the beam on the biological single crystal. The HRPD machine is one of the most crowded and most productive machines we have, so if the four-circle machine does not cause much loss of the beam that will be okay but I am afraid it might. So we are now to think of the number of beams itself. Though it is only a few years since the new reactor started, we are now coming short of beams and we should think of the future beam again. That is a problem which we must always think of.

Another thing which we are considering is upgrading of wide-angle neutron diffractometer WAND which we have at HFIR at the Oak Ridge National Laboratory since about ten years ago under the US-Japan Neutron Scattering Collaboration Program. The diffractometer looks as in this figure and we have used it to measure time dependent structural changes as well as the two-dimensional diffraction patterns. This view graph shows diffuse scattering of manganese which was measured with that machine at different tilting angles of the diffractometer table so that we can measure different slices in the reciprocal space. In principle we are measuring three-dimensional diffraction of the diffuse scattering. We are upgrading the detector now, and if we have in future a very high intense beam, I hope, we can add something more to analyze the energy and then we will be able to measure two-dimensional or even three-dimensional inelastic scattering. Thank you.

CHAIRMAN: Thank you, Dr. Funahashi. Okay, let me stop for a while here. We have already covered some aspects of the steady source problem, the one was presented by Dr. Hayter, which is associated with big future prospect concerning ANS. The other is related so to speak to a successful upgrading of the present JRR-3M. So anyone is welcome to join the discussions, panelists and also the audiences.

ARAII: I would like to have some numbers from Dr. Hayter. First, how much is the fuel consumption for such a big reactor? Second, if you replace the fuel, how long does it take. Then third, how much is the running cost? We know the nominal construction cost but probably nobody discussed about the running cost, so would you tell me that?

HAYTER: Sure. The fuel on loading is 18 kg. We could load the fuel element with up to 100 kg in terms of space available. What limits the length of time that it can run is the build-up of the oxide on the aluminum plating on the fuel which affects the heat conductivity. And at the moment, for the 330 MW design, that gives 17 days operation, with four days for refueling. The running cost is about ten percent more than the running cost of HFBR and HFIR together, that's about $70 million a year. And those two reactors will be shut down when ANS starts.

RAUCH: Is there an estimate how the cost increases with the flux available? Because we face also sometimes the argument why not build, let's say, five ILL reactors, then we have in principle the
same number of neutrons available for our experiments and perhaps even more users can attend that. Also costs and prices.

HAYTER: Yes, the price/power relationship for nuclear reactors is very well known. Price scales as the power to the 0.6 exponent. But that's only if you are doing a good design job.

Now, if you simply copied ILL, we've done a lot of estimates on things like that because a lot of people asked that question. The ANS will cost $1.7 billion in 1992 dollars in what is called line item money. To rebuild ILL without touching anything, no change at all, I mean you will be very tempted to make all sorts of improvements, but not touching anything would be about $1.4 billion in the United States today. And the reason is the regulatory requirements that didn't exist when ILL was built.

To rebuild HFIR would be similar amount, not quite as much but similar. So if you reduced the ANS to 100 MW like HFIR then you could build that for about half cost, but you wouldn't have cold sources or any of those things. I am talking about the exact copy.

RICHTER: While we are discussing cost, maybe I should just add another number. We have undergone a study on what it would cost to build ORPHEE reactor complete with instrumentation in Germany under German regulations and the price of this would be about $200 million. So you see, there is a very large leverage.

HAYTER: But that's just for the reactor, detritiation and everything. You see, that's $100 million by itself.

TAYLOR: John, what's the critical bit of technology in ANS?

HAYTER: There isn't. The first rule we wrote down to the project is no new inventions. We have to meet the minimum requirements of the scientific community with the present day technology. We have seen so many projects fail totally because they needed a new invention like a better superconducting magnet and it didn't happen.

Now, we have spent about $30 million so far trying to get every advantage we can, to go beyond current technology. But we need no new invention to produce the fluxes I showed you.

RICHTER: Having this new flux you must have problems of irradiation. So what are the standing times for the most exposed components of this reactor?

HAYTER: The central pressure tube around the core requires replacement probably about every 18 months. Beam tubes will be about every 2 years. So the entire reactor is being designed for very easy maintenance and replacement. And in fact those three-dimensional pictures I showed you are not shown for artistic purposes. We have a very sophisticated computer design system which takes the two-dimensional engineering drawings for the entire reactor and builds the three-dimensional object and there are two points in doing that.

The first is that you never on something as complex as that get it right the first time. But much more importantly, is having built the complete reactor in three dimensions, you can enter it to take out any given part and see how to do it. And you can then find that you may have built something which can be put together, but you cannot take out a beam tube for some reason you've never thought of. So we are doing a lot of studies to put the whole thing together and take out each part separately. This is lot of work and we have a whole team, a full-time team of about 20 people, looking at maintenance questions and how to minimize down time.

CHAIRMAN: Okay, let me stop the discussion now about the steady source at this point because we have already run over the scheduled time.

Part 2

CHAIRMAN: So let's move on to the discussion of Pulsed Source. The first speaker will be John Carpenter from ANL.

CARPENTER: Let me say to begin with, thank you to our hosts for providing us all such an interesting meeting and such comfortable surroundings. I want also to thank the Chairman for providing me this opportunity to describe a project, that is the IPNS Upgrade at such an early stage in its evolution.

First I would trace some of the history that led us here. Gerry Lander already indicated some of this in his talk. The IPNS Upgrade is a 1 MW, 2 GeV synchrotron operating with half a mA of current at 30 Hz feeding two target stations and providing 36 neutron beams.
This has come out of the history that started roughly in 1984 with the meetings of the Seitz-Eastman Committee. That Committee recommended four large materials science facilities in this order of priority: to build a 6 GeV photon source; advanced steady state neutron source, a 1 or 2 GeV photon source and an advanced pulsed neutron source.

Things have not been done in that order. The Advanced Light Source has been completed at Lawrence Berkeley Laboratory, the Advanced Photon Source is well under construction and will be finished in about three years at Argonne Lab, the Advanced Neutron Source at Oak Ridge has come through an extended period of conceptual design. There has been no action on the recommendation about the pulsed source until very recently.

Now, the news has come since I first compiled the information on this slide that the Advanced Neutron Source is happily in the budget for 1994, as Dr. Hayter has said. So we are very pleased with that and now hoping to get on with the questions of the pulsed spallation source.

More recent considerations have stemmed from the announcement last June of the high cost of the Advanced Neutron Source. This is a matter of, say, appearance rather than the reality. It is a large amount of money that was more than was expected, which caused the Department of Energy to convene a new committee headed by Walter Kohn to review the recommendations about the reactor. Those considerations were completed and the conclusion was that the first priority is to complete the Advanced Neutron Source. We see that this recommendation has been taken to heart.

The second priority is to develop proposal for 1 MW for pulsed spallation source. And I am here to describe briefly some of that activity.

Just now, there has been granted about $5 million in the next year's budget for pursuing design, controlled by a Central Design Group at the Lawrence Berkeley Laboratory. We don't know exactly what that means — the arrangements are now just being worked out — and in the meantime we have been working on the proposal as a feasibility study for the IPNS Upgrade.

Now I will tell you a little about the basis for our choice of parameters. First of all, the 1 MW came from discussions of the spallation source and accelerator and target technology groups within the Kohn Committee, who said, "We think 1 MW is something that can be done", which set the basis for further works.

I would outline the scope of our project a little bit more. We have taken this further in the case of Argonne's specific proposal. The project involves a 400 million V Linac, a rapid-cycling synchrotron of 2.2 GeV, 2 target stations with proton beams incident horizontally on the target. Instruments for neutron scattering numbering 24 are to be provided in the project. The cost of the project would be about $400 million.

The time from start to beginning of commissioning is about four years and much use will be made of existing infrastructure and buildings at Argonne Laboratory valued about $100 million. All these ideas are in the process of being refined as I speak to you now.

This is what the layout of the IPNS Upgrade looks like. All these buildings exist. Here is IPNS as mentioned. Here is the shielded ring for the old 2GS, which was a 12 GeV low current machine. It is just right for 2 GeV high current machine. You might say why, if you could get a 12 GeV machine in there, is there needs now for only a 2 GeV accelerator. The answer is that you need lots of straight section space for RF and other instrumentation in a high current machine. And this is a one-megawatt facility.

Two large buildings exist, which are just right to accommodate 2 targets each with 18 neutron beams and the associated instruments.

Now, I would like to return to some of the preliminary considerations that underlie our choice of parameters. The neutron production rate, the gross neutron production rate has been thought for a long time to be proportional to the proton energy less 120 volts, what you might call the "E minus 120" rule. It is also true and I will show you a little bit more of that, that the neutron production rate density per unit of target surface area decreases a little bit when the proton energy goes up. But the thermal power density, which is the design limiting factor, decreases also when the proton energy goes up. The first is a disadvantage and the second is a designer's advantage.

We also did a rather lengthy study which probably has to be repeated again and again before everyone is satisfied. Our instrument scientists combined in an effort to conceive instruments appropriate for 1 MW pulsed source. This determined what we want for frequency, that is the lowest frequency, or highest frequency that these instruments will stand when we design for 1 MW beam. This led to a division into two classes of instruments, those that would run on a 30 Hz source and those that would run on the 10 Hz source. So we multiplexed the beam at 10 Hz to one target and to
the other in sort of an iambic pattern, "dada dada dada", so that to the two-thirds of the power goes to the high frequency target and the low frequency target gets one-third of the power.

Now to illustrate some of these questions of power density, the neutron production rate and so on. We have a peculiar situation in that our codes, the ones that are used classically in these designs, are not certified to work above about 3 GeV. So we've done computation up to 12 GeV just to show the picture and here are the results.

The maximum outgoing neutron current in terms of n/cm²-sec, reaches a maximum just above 1 GeV and of course, according to the E minus 120 rule, is a very small number for low proton energies. The total thermal power is always about 60% of the beam power. The maximum power density is actually somewhat decreasing all the way up to 12 GeV. Probably it will be interesting for you to see how this turns out in more detail.

This gives the axial profile of the power density distribution, here shown on a logarithmic basis. For protons above about 1 GeV, there is hardly any difference among the curves. Therefore the accelerator designers are more or less free within that range of energies to choose what are the best parameters from their point of view. The target designers would be about as well off in every case. Actually 800 MeV protons are a little bit too low in energy, which leads to somewhat higher power densities than the other energies.

Here are the two target stations in more detail. We actually have the inners worked out pretty well. The diagram shows the neutron beam lines and footprints of typical instruments. This is done, I think, in the classical way, that is, you are not to believe that these are necessarily the instruments that will go there or that they are exactly where they eventually will be, but they represent a feasible arrangement which is what we need for this stage of the design study. This is 30 Hz, (actually 20 Hz) target and this is the 10 Hz lower frequency target.

We are making use of a split target arrangement, which makes it possible to have six differently optimized moderators in each of the two target stations. Three beams are brought out from one surface of each of the six moderators. Four moderators, that is two in each facility, are of tall configuration, which is called for in a number of instruments, 20 cm tall rather than the classical 10 × 10.

So I just continue one level at a time to get you deeper and deeper into the picture. This figure shows 2 targets in terms of the way that the engineering has been worked out. We've calculated the power loads, the temperature profile, the stresses in the flow rates and, in short, have done all the engineering calculations. The target is a stack of tantalum plates which are progressively thicker and thicker the farther into the target. The front target has an independent cooling system and the plate thickness is governed by the requirement that there will be no local boiling on the surface of the plates. In the back target the design is constrained by a maximum center temperature, 550°C. It turns out that the total neutron production rate from the front half and the back half is about the same as it is divided, and this will ultimately be optimized more carefully.

I will just go to one last figure showing you higher a level view of the target system. This diagram shows 2 m thick gates, a solid central core of iron shielding and an outer shield of concrete. This is designed for dose rates such that the experiment areas can be continuously occupied. The shield is about 6.5 meters thick. With that I think I will yield to the next speaker.

CHAIRMAN: Thank you very much, Mr. Carpenter. Now, let's go to the next speaker, Professor Watanabe from KEK.

WATANABE: Thank you, Mr. Chairman. The construction of a high-power proton linac called ETA (Engineering Test Accelerator) is being planned by the Japan Atomic Energy Research Institute as a part of R&D plans for an accelerator-based rare actinide transmutation system (OMEGA Program, Science and Technology Agency, Japan/OECD NEA). The accelerator can also be utilized in basic science. An intense spallation neutron source for condensed-matter science is a typical application. This will provide an opportunity to realize a MW-class pulsed spallation neutron-source. We would propose this as a next-next-generation (post JHTP/KENS-II) pulsed spallation neutron source in Japan. We discuss here the possibility of realizing this idea.

The specifications of ETA are as follows: 1.5 GeV, 10 mA in time-average current, 100 Hz, pulse length of 1 ms, duty cycle of 10%, beam power of 15 MW.

What kind of neutron source can be considered using the proposed proton linac. The first option is of the SINQ type, in which the pulse structure of the proton beam is completely ignored. From simple scaling one can expect a maximum time-averaged thermal neutron flux of the order of
$3 \times 10^{15}$ n/cm$^2$-sec, provided that a compact high-power target comprising of low neutron-absorbing heavy metal(s) can be developed.

The second option is of the SNQ type, in which the pulse structure of the proton beam can be utilized to some extent. However, the longer pulse length (1 msec) may decrease the merits of a time-modulated neutron source, as considered with SNQ. Further R&D studies concerning the target engineering will be necessary in order to utilize a higher beam power (15 MW).

The third option is a neutron source based on muon-catalyzed fusion ($\mu$CF); this type, however, is more or less in a state of art. The energy cost to produce one muon (about 10 GeV) and a cycle rate of about 100 (one muon can catalyze the D-T fusion reaction 100 times) have already been confirmed. Although the energy cost is larger than that in the case of a spallation neutron source, the heat generated in a muon production target can be removed separately from a $\mu$CF target. We assumed a spherical $\mu$CF target having a radius of 20 cm in a large D$_2$O tank as SINQ. Although the neutron energy is higher (14 MeV) than in the case of spallation, it can be shown by a simple calculation that this neutron source can provide a maximum time-average thermal neutron flux of about $2 \times 10^{15}$ n/cm$^2$-sec.

The three options mentioned above require full-time and full-beam from the linac, if we are to aim at realizing one of the best intense neutron sources. It is, however, not realistic since the first priority of this linac is nuclear transmutation. We must therefore find a compromise in the beam intensity and/or the beam time. Such a compromise would make the new source less attractive.

The fourth option is a pure pulsed spallation neutron source. In this case $H^-$ beam acceleration and a compressor ring become indispensable. Generally, the simultaneous acceleration of $H^-$ beam along with protons is feasible. One of the most important specifications is the beam current which can be obtained from an $H^-$ ion source within the required beam emittance. In the linac considered for the Japan Hadron Project (JHP), rather modest, but more realistic, parameters (1 GeV, peak current: 20 mA, emittance: 1 mm mrad, pulse length: 400 $\mu$s, chopping factor: 0.5, repetition rate: 50 Hz) are assumed. A time-average beam power of about 0.2 MW can be obtained under these assumptions. For a 1 MW beam, the typical specifications, as 1 GeV, peak $H^-$ current: 65 mA, pulse length: 500 $\mu$s, chopping factor: 0.65, become necessary. At present, no $H^-$-ion source is available which can satisfy such specifications.

Although the detailed design for ETA has not yet been completed, we can compare here the parameters for ETA with those for JHP. One advantage of ETA is a longer pulse length (1 msec), which produces a higher beam power with a given peak current of the $H^-$ beam. With the modest peak current assumed in JHP (20 mA), we predict that a time-average beam current of 1.3 mA is possible. Since ETA will have FR power supplies with a higher power than those for JHP, acceleration of $H^-$ beams at this intensity will be easy. The maximum beam current acceptable in a compressor ring is determined by the space-charge limit. The present current is below this limit. If we can expect a higher peak current of the $H^-$ beam (say 60 mA) in future, the average beam power can be increased up to 6 MW. In this case two identical compressor rings would be necessary.

We are keen to realize KENS-II (a part of JHP) as soon as possible. However, it has unfortunately not yet been financed. We are proposing a phased program for KENS-II while aiming at an earlier realization. Although the present proposal is independent of KENS-II, various possibilities for a future intense spallation neutron source should always be considered. In conclusion, if ETA is realized for the R&D of the nuclear transmutation techniques, we can consider one of the best pulsed neutron sources early in the next century.

CHAIRMAN: Thank you very much, Professor Watanabe. Dr. Mizumoto will supplement the comment.

MIZUMOTO: Thank you, Mr. Chairman. Since Professor Watanabe kindly introduced our project, I would like to stress close collaboration between nuclear engineering and accelerator technology. The size of our accelerator is expected very large based on the requirement for the nuclear waste transmutation. Maybe, the project will be realized after 2,000 year.

Anyway I would like to show a little bit the works by presenting some examples in the collaboration of the nuclear engineering and accelerator field. I will not discuss about the OMEGA Project in detail, the OMEGA Project is the Japanese national project and the proton accelerator based
transmutation is one of the options which have been studied intensively among the nuclear engineering people, chemists, physicists and also accelerator people.

This viewgraph shows the relationship between the accelerator technology and nuclear engineering. The nuclear engineering is divided into the fission part and fusion part. This viewgraph is made using Chinese characters but sometimes one of the nice things to use Chinese characters is that it can contain various concepts in a short single character.

I hope the foreign participants to memorize that the Chinese characters of our favorite neutrons. This is the ion source, etc. This is the region where the accelerator technology and fusion people can work together, such as ion source, ultra vacuum, high power RF radio frequency, superconducting, electromagnet, etc.

This is the field between the fusion reactor and the accelerator, including radio isotope production and radiation therapy. This is where people from these fields are concerned; control, operation and maintenance, robot, radiation monitoring, shielding, the construction of building and tunnel etc.

Of course, the target part is a common part where the nuclear engineers specialize, for example, the neutronics calculation, radiation damage and heat calculation. This is our accelerator-based transmutation target concept, which is very similar to the FBR, first breeder reactor concept.

This is the front end of the intense proton accelerator now being developed. This is the ion source which we cooperate with fusion people, neutron beam injection (NBI). This ion source was constructed and already tested with the current of 140 mA at 100kV. We believe that this ion source is one of the best high duty ion sources in the world so far for the accelerator.

This is the vacuum tube (tetrode) for the RF source which was developed as the JT 60 RF heating device. Now we are trying to use this tetrode for BT8 accelerator. The design is completed and fabrication has already started.

Of course, the main item of our development is the accelerating structure. The first one is the calculation of the three-dimensional electromagnetic field in the structure and the next one is the three-dimensional calculation for the heat distribution. This kind of calculation is common in the nuclear reactor engineering. The large displacement in this picture is calculated to be several μm.

Measurements of basic nuclear data are very important. One of our groups are measuring the neutron spectra using a very large target assembly at KEK 500 MeV booster proton synchrotron facility. In order to get a very good information about neutron distribution, the result is checked with the calculation by the code system.

In many fields, people who are in the reactor field are experienced for these kind of common important technologies, in particular with regards to reliability, efficiency and also safety operation.

Thank you.

CHAIRMAN: Thank you very much, Dr. Mizumoto. Let me stop here. We have now covered rather promising future view of pulse reactor source. Of course, with close collaboration between nuclear engineering people and accelerator people. The floor is open for discussion.

ARAI: At first, Jack, could you tell me the running cost for such 1 MW source.
Carpenter: I cannot exactly because that is being worked out in the process of our feasibility study. We have made an initial guess, namely something like $30 million per year for periods of approximately 36 weeks per year.
ARAI: Then next, Professor Watanabe, could you tell me how feasible is the μCF neutron source? Because you need the target to produce muon itself. So, of course, by that target you can produce neutron. So I think things are very complicated for such neutron source.
WATANABE: Essentially, the technology isn't still established, but the major part of the heat generation is inside the muon production target, not in the neutron production target. The total energy release per fusion is about 17 MeV, while about 14 MeV is removed with neutron. The heat generation in the neutron generation target is rather modest compared to the heat generation inside the muon production target.
ARAI: But you said the neutron flux from the μCF source is still less than the spallation source. I don't know much about it, but is it real?
WATANABE: I think so at this moment, but in near future, if one can control He-3 concentration in tritium, then the Xc (cycle rate), which is now 100, can be increased to 200 or 300. I don't know whether it is possible or not. But at this moment the efficiency of the spallation source is better than the μCF neutron source.
ENODOH: I have two questions to either Noboru Watanabe or Mizumoto-san. If you consider this project where is this construction site going to be. That's one question. The other thing is probably to Noboru Watanabe. You said pulse width is a little bit longer than what we need.

WATANABE: No, the macroscopic pulse duration from proton linac itself is longer than that designed in JHP but that from the compressor ring is the same.

MIZUMOTO: About the first question, I think it is a little bit too early for us to say the exact place, but in principle, the length of the accelerator may be around 1 kilometer, so it is possible to install the accelerator in the Tokai site. Of course, that will be in the underground tunnel.

CHAIRMAN: Dr. Taylor, I guess you have something to say. No?

KAJITANI: Jack or somebody else. Several times I have read the report according to the spallation neutron source, saying that the basic object to generate more intensive neutron pulse is at the cooling system, the target design. If you will boost the acceleration voltage or current, the real object to boost the neutron intensity is at the design of the target itself. Somebody were saying that the target could be the liquid bismuth or somebody was saying about the water cooled tantalum that you were saying. I would like to know what is the present maximum neutron production due to the spallation source and the near future target, or maximum neutron production expected in near future.

WATANABE: The target engineering problem would be common to the ESS and Carpenter-san's IPNS upgrade. Almost the same problems we have. Probably up to 5 MW target, the solid state target can work I think. But anyhow, very critical. Of course, there is another option to utilize the liquid metal target.

Still, I think, in the range of present engineering it is possible to construct 1 MW spallation source. Of course, we need extensive R&D.

CARPENTER: As we have identified some materials questions even at the level of the 1 MW target, there would be an attractive question to you, Kajitani-san. Hydride formation in tantalum target material may cause embrittlement and difficulties in management of thermal cycling stresses even at the 1 MW level. This might mean that other target materials should be considered. We need a greater database on, say, tungsten alloys and on some of the alternatives in this kind of application, namely platinum and gold. So there is, even at the 1 MW level, a need for R&D and further determination of where problems lie.

CHAIRMAN: Thank you. Any other comments?

Part 3

CHAIRMAN: Okay, I had better go on to the last topic, which is related to software aspect. The first speaker will be Dr. Bruno Dornier.

DORNER: Thank you for having me here participating in the conference and the Panel Discussion. I would like to start with a rather young photograph of the site in Grenoble where you see the high flux reactor of the Institut Laue-Langevin and on the same site the 6 GeV European Synchrotron Radiation Facility. In this synchrotron radiation facility there will be an instrument for inelastic scattering with very high resolution on one of the beams in the second generation.

I collaborated in the first experiments which were performed at the storage ring DORIS at HASYLAB in Hamburg. There we measured longitudinal dispersion curves in beryllium, where the resolution was in the order of 55 meV. Now the colleagues there brought the resolution down to about 10 meV which means in order of 10^{-6} of the X-ray energy. This inelastic scattering will be limited to high energy transfers of 50 meV and higher.

I will show you how it works. Here you have a sketch of the instrument. The beam comes in through the double monochromator which takes the heat load of the white beam. The essential part is a monochromator focusing in almost back reflection on the sample position and there is again back reflection on the analyzer into the detector. The high resolution in back reflection is given by the penetration depth of the beam into the crystal. One advantage of inelastic X-ray scattering lies in the fact, that high energy transfers can be examined at small momentum transfers, because the X-ray wavevector is almost constant in length at energy transfers very small compared to the energy of the X-ray beam itself with more than 10 keV. In the case of neutrons with thermal energies the change of k with energy transfer is considerable and therefore the momentum transfer at small scattering angles is necessarily connected to this change of k. Thus inelastic X-ray scattering is particularly useful in Brillouin scattering from liquids.
A disadvantage in X-ray scattering is the sample size, which may be smaller than you wish due to absorption. The active volume with which you can interact may be the limiting factor for inelastic X-ray scattering. In conclusion these two techniques are complementary.

And now, I want to make some points on inelastic scattering with neutrons where there are many aspects. Here I would like to draw your attention to the possibility to measure very carefully integrated intensities of phonons. Out of many of these intensities one can determine what is written here as SIGMA. SIGMA is the amplitude of an individual atom within one mode. If you do that for all the atoms in the unit cell, then we call that the dynamic structure determination or the eigenvector determination for a particular phonon.

As one example on which we worked take silicon which has two particles in the unit cell. The wave travelling in space diagonal, the [111] direction, has one open parameter. The amplitude for the first particle, and the second particle has a phase shift which is partly given by the distance.

But besides this natural phase shift, the overall phase is not determined by symmetry. The phase shift is given by symmetry - to be zero - only at the zone center and the zone boundary. The results of measurements performed by my colleagues and myself in 1990 were able to eliminate three different lattice models by this technique. It turned out that the bond charge model was the best one because it not only describes the dispersion curves equally well as all the others models. But this eigenvector determination represents the crucial test that the bond charge model was the best.

In the meantime, my colleague Jiri Kulda came last fall to JAERI and worked on the instrument TAS-1. He repeated the eigenvector determination. The black dots are new data obtained here in Tokai with a somewhat different technique. I do not go into this detail. The results coincide with previous ones.

At the same time theory advanced. The dashed curve is obtained from the bond charge model and the full curve from "ab initio" calculations. The latter one is a pseudo potential calculation in which one puts as much knowledge of the bond structure of the electrons in silicon as possible. So here, I presented progress in the understanding of the lattice dynamics of silicon.

Now a short word on polarized neutrons. An interesting problem which has been studied long ago without polarized neutrons and recently with polarized neutrons is the lifetime of magnetic excitations in the quasi one-dimensional substance CsNIF₃. Here is the dispersion curve in the phase without long range order. The lack of long range order is reflected in an uncertainty of the origin of the dispersion curve. The resulting width of the experimental signal is larger than the width corresponding to the true lifetime of excitation. In 1975, without polarized neutrons, we were able to identify two components of the width corresponding to the two time scales. But we could not study them in detail. In 1990 we performed an experiment with polarized neutrons at the ILL together with my colleague and friend Kazu Kakurai from the Institute for Solid State Physics, the University of Tokyo. By means of spin-flip and non-spin-flip we can separate the narrow component which is related to the real lifetime from the broad component which is related to the uncertainty of the origin of the dispersion curve.

My last transparency shows the widths versus wavevector q. The width from disorder is broadest there, where the slope of the dispersion is steepest and extrapolates to zero at the zone boundary, where the slope becomes horizontal. The width from the true lifetime is smaller and exhibits an irregularity at about q=0.3. This irregularity was predicted by George Reiter as an anharmonic effect arising from a particular multimagon interaction.

In summary I would like to make the point that inelastic scattering will remain a strong domain in neutron scattering. In particular I suggest one should continue to develop polarized neutrons because I think that this is the power of neutron scattering in the future. Thank you very much.

CHAIRMAN: Thank you very much. This will be followed by Professor Fujii.

FUJII: I just use only two viewgraphs. Let me stand on the user's point. Neutron used to be only one field which required big facilities except for the high energy physics. Now, the synchrotron radiation comes in as an enemy or a friend. So we can see very similar structure in both neutron and synchrotron radiation society as shown in the next viewgraph.

The neutron community consisting of users on both sources is aiming at a small science, as already mentioned by Gerry yesterday. So neutron community constitutes reactor-based users and accelerator-based users. In the case of synchrotron radiation community, on the other hand, this community consists of X-ray people and VUV people.
The contrast is that every neutron is good neutron in this neutron society but every photon is not necessarily a good photon in that synchrotron community. You can see these directional vectors. As far as this longitudinal direction is concerned, they are friendly. However, in this transverse direction they are competing each other particularly in the case of a budget, to get the higher priority to construct their own machines.

However, for all of us based on such a big facility our base is not so stable in a sense that we may encounter a very difficult time without neutrons or photons due to unexpected shutdown. Therefore, what I would like to say for future prospect not only in neutron scattering but also in synchrotron radiation community is that we should be friendly once our friend’s machine is shutdown unexpectedly or even as scheduled, and we should give our hands or rescue to our good friends. That is my point I would like to say. Thank you.

CHAIRMAN: Thank you, Dr. Fujii. We will go to the next speaker, Gerry Lander.

LANDER: Well, I had a chance yesterday so I won’t say very much. I wanted actually just to follow up on Professor Fujii’s nice remarks there with the arrows because about four years ago, I started getting involved in this synchrotron business and I found it to be very stimulating and very exciting and we are certainly looking forward to the new sources, but also very frustrating.

Most of the things, not all but most of the things we have been doing have been connected with magnetic scattering of X-rays. And actually we’ve been using resonance magnetic scattering which has a very large intensities. But the trouble is the penetration has been very small and you notice here that with beams presently at Brookhaven of 1 x 0.5 mm^3 our penetration is less than 2,000Å. This has resulted in as looking at 10μg of these materials which is not much.

The problem is that the magnetic properties in those skins, as Gen Shirane said on the first day of the Conference, can be very different from the bulk behavior. We have found to our great interest, but also frustration, that after we do these experiments we have to take the same crystal and go to neutron source. In fact, last week, I was at Brookhaven doing one of these experiments and we wanted to go to the Brookhaven neutron source but, alas, it was shut down. So it is very frustrating for us there. It was actually the first priority of this experiment which has got some very interesting results which I won’t talk about.

The idea of having them both on the same site is going to make, I think, a tremendous impact on this neutron community in the future. And we should be running workshops, and educational events to emphasize the duality of these two microscopic probes and that one can use both.

We’ve had two workshops, one organized by myself and others and another one organized by the amorphous and glass people in Grenoble recently, and they have both been sellouts in the sense of people from the other community trying to learn what you can do. So I think that breaks down some of the barriers. One of the reasons I went into the magnetism with X-rays was that I had hoped to see if I could make some of the synchrotron people a little more honest by going in there with some knowledge about neutrons and I am happy that I think that has happened, myself and other neutron people going in there.

Now, I wanted to address a second question in this very short time and it goes back to what I said yesterday. And it is really related to this viewgraph that I showed, which is what I call the economics of supply. There are about 40 sources presently in the world doing neutron scattering. Of these 40, 36 are reactors and their number will reduce. So we have to, I think, address this problem of the feed-through of new ideas. As John Hayter mentioned this morning, because we don’t have the luxury of the huge increases of flux as in synchrotron radiation, we have to set the tone to encourage creativity. So, how can we guarantee or have mechanisms to continue this creativity. I mentioned educational aspect. Now, Noboru Watanabe raised the question to me, "Can you expect the budget to just go on expanding?" I think that’s a bit unrealistic as well. I would like to propose that we tried to do two things, one is re-establish more formal ties between the large sources which will continue to be built, of course, and the smallest sources which will then undoubtedly decrease in numbers.

The second one is to insist on investment in the community. The Japanese neutron scattering society and NSSA in the United States have some method for insisting on a 10% investment so that we are going to guarantee having new ideas.

You see, in the synchrotron community, its really different because there is a home sources and they have more beams. So that I think we have to make some mechanism right now to guarantee that the large sources and the few remaining small ones work together in a way which continues to give
us this base of new ideas and creativity in the future. Because otherwise I think this field is in trouble.

CHAIRMAN: Thank you very much. The next will be the last speaker, Professor Endoh.

ENDOH: As the last speaker as well as after the excellent promoter of Gerry Lander, I feel a difficulty but I wish to finish my task.

The key words for my talk are the complementarity, the sample preparation and the optimization of the instrument and technique.

As I already showed a viewgraph in my talk at the first day of the conference, we need both pulsed spallation and steady neutrons in order to complete the spin-wave scattering studies in $\text{La}_2\text{NiO}_4$. We need spallation neutrons to produce the spin-wave dispersion curve but in order to study the spectrum of the scattering or the intensity profile of the scattering, we need steady neutrons, since the triple axis spectroscopy is well ahead. With the combination of these two independent experiments with two different neutron sources from an identical crystal, we can compare the experimental results with the existing theories precisely. From this example, we give the first message that we should enjoy the complementarity of pulsed and steady neutrons.

Let's go on the second point. This example is also shown in the last talk. We now know the large single crystal for the study of the high temperature superconductivity by using neutrons. In order to obtain the large crystals of cm size, we have worked hard for more than five years since we started from the tiny one with less than mm size. Why we could achieve is very interesting. I emphasize here that it is not good enough that you only ask the crystal grower. Instead, you must be corporate to them, you have to encourage them and you have to communicate with them. This is the points for the success, which is the second message.

Then the last one is the optimization of the instruments and techniques as well as matching your problem to the neutron source. As I learned a lot of these things from Gen Shirane, we should present the best data with the low background or the best signal to noise ratio by your best effort. We had better not to present data of only signal with cutting the back ground. Then people will convince us more and get a message that the neutron is beautiful.

CHAIRMAN: The last topic was on software aspect so it is very difficult to wrap up the discussion. Certainly, complementarity is one of the big topics. But there are some other topics included. Anyone can make discussions or comments on these various aspects.

RAUCH: I do not know exactly how to comment on what Gerry Lander said that the number of the small sources certainly will be reduced in future and I do not know whether this is perhaps a very dangerous statement because, as you have said, many ideas have come from the smaller sources and I think not only ideas are coming but also students are coming.

So when we cut the space at the universities, I think it may become quite difficult for the future. For instance, if I think synchrotron people never would say that there will be in future less X-ray sources at the university level and students need to be trained on that home base sources. And I am somehow afraid if there is no possibility during their education to include them in neutron techniques. It may come not only a problem for the smaller source but also for the large facilities.

LANDER: I agree completely. I am certainly not advocating this as a policy, but the smaller centers are in financial and regulatory difficulties. That is just a fact. Look at Austria.

RAUCH: May be they operate or things like that because I think reactors as we have learned before, I think that was a very nice contribution from the Japanese side, are really used for most cases also for other purposes. And so we cannot use all the costs which exists to the neutron scattering. So they are needed for many other purposes and educational ones, too.

So I think that at least to maintain the operation or making a proper upgrade should be possible in any case and it happens quite often.

LANDER: Well, I very much hope so and I think the Japanese model may well be used in other countries is one of the points I made yesterday. I hope it is because I think it is tremendously successful model.

TAYLOR: It is very difficult for every individual university to have its own neutron source, unfortunately. But we should be aware of this and something that Gerry, I think, pioneered tremendously well in the States and in 1980's when he was at Argonne, that was the use of
workshops and education. We should never forget that we have to educate the new generation. Each year there is a new generation coming up and we must educate them.

And those of us who have big facilities have owed to the community to provide the infrastructure and the availability on the sources to do that education. Otherwise we will die. **Cookson:** Australia sounds very much like Austria and as a strange coincidence we have similar situation, really. We have what used to be called high flux reactor and it is also quite old, but I just like to throw in my support for that last comment that some fluxes are a lot better than no flux and I myself did a lot of PHD work on triple axis machine that was obsolete by international standards now. But it's the job that serves its purpose and as such I would not have had that access to overseas facilities that I had in Australia.

**Hutchings:** I just wanted to ask the Panelists' opinion on the topics investigated by neutrons. Gerry showed the Gaussian distribution of topics with the middle holding up, well, I am sure there are lot of exciting areas in material science which haven't been explored yet. But I do feel that the really big area totally unexplored is biophysics area either with neutrons or synchrotron radiation and I wondered whether that was where we should look for the bigger square of new users.

**Landar:** Well, I have been on committees looking at the biological uses of neutrons. It seems to me very dangerous. We've been promising, Joe has been promising, or not promising, the use of solving all the problems with neutrons. He covered that, of course, in his talk.

**Zaccai:** It is very difficult to attract users and biophysics area in neutron scattering when today there is nowhere in the world except perhaps one place where experiments can be done, the place the experiments can be done and are being done is Tokai by Nobuo Nishimura.

We have tried to do experiments at places like Risø and Saclay and I do not want to malign my friends at Risø and Saclay but the instruments are super-saturated. They do have instruments which could be used for biology. At every meeting they say "our instruments will be useful for biology because politicians want to push the life sciences" but when we go and ask for time they say, "we prefer to do five polymer experiments rather than ten biological experiments" when you talk to the people. So as long as you don't have people who are interested, then you will not be able to train other people and you will never have people interested when there is nowhere where work can be done at the moment. Since the shutdown of the ILL there really has been no place where a reasonable number of experiments could be done to make things worth while.

**Landar:** Therefore, I think new sources?

**Zaccai:** Certainly.

**Chairman:** John, you were going to say something?

**Carpenter:** Yes, may I? Concerning a number of comments that had to do with the sorrowful situation in which we see small reactors are being shut down and access to facilities that provide for methods development diminishing. I only mean to call to your attention that there are some yet undeveloped prospects for small scale accelerator-driven neutron sources that might serve in a similar role to the way the back room X-ray sets do in most chemistry departments.

This is an unevaluated set of prospects but I think it needs to be recognized and given some attention.

**Chairman:** Any other comments? If not, I would like to close this session.

I think it is the role of the Chairman to make some sort of wrap up after this kind of Panel Discussions but I understand it is a rather difficult job for me. Personally I feel that way at least.

As far as advanced sources are concerned, we are going to be having a good prospect for the future. On one hand, we have the good expectation for the coming ANS. On the other hand, we do have a good prospect for the 1 MW or 2 MW accelerator source as the pulsed source. In that sense, we are still going on to push forward the new performances as neutron sources. I think our future is very promising in this respect.

The soft wareaspect is very difficult for me to pick up right words. Certainly, some sort of general agreement seems to exist that there must be complementarity and competitiveness coexisting in between pulse source and steady source as well as in between X-ray and neutron.

This kind of competitiveness between the different fields may be considered as advantageous, rather than disadvantageous, to make the progress using the stimulation provided by their opponent's power. I think this aspect will also provide another very promising future view.

I think each of you must have gotten your own impression from each speaker's presentation. Since the time has run up, I would like to close this session.

Thank you very much.
Summary Talk

Toyojiro Fuketa
Japan Atomic Energy Research Institute

Distinguished Guests, Ladies and Gentlemen:

On behalf of the JAERI, I sincerely thank all the speakers, chairmen, participants, Organizing Committee members, Secretariat staffs and interpreters for their contribution, support and cooperation in making this Symposium a success.

Only two years after the discovery of neutrons in 1932 by James Chadwick, Enrico Fermi had already tried the slowing down of neutrons and transuranium element production. Only four years after the discovery of nuclear fission in 1938 by O.Hahn and F.Strassmann, the first self-sustaining chain reaction was achieved in Chicago Pile No. 1 by Enrico Fermi et al. at the University of Chicago on December 2, 1942. This quick progress is really fantastic.

Use of neutrons as microscopic probes was much promoted by the advent of research reactors, and it has been further developed by the advancement of higher flux reactors and various accelerators. But historically, quite a few research efforts to use neutrons had been made much earlier than the advent of research reactors. In the discussion period at the end of Session I, Prof. Ryukiti Hasiguti, Prof. Emeritus, University of Tokyo, told us that he and his senior co-author Prof. Motoharu Kimura, Prof. Emeritus, Tohoku University, made neutron scattering experiments on phase transition of metallic alloy, order-disorder change, thermal strain of quartz, and so on, by using a radon-beryllium neutron source in the early 1940's. This work was published in the "Proceedings of Japan Imperial Academy" and the "Proceedings of Physico-Mathematical Society of Japan".

The first Keynote Lecture by Prof. M.Date, Osaka University, was composed of (1) a comparative study of the condensed matter physics research with neutrons and with other microscopic probes, (2) new expected frontiers for study with neutrons, and (3) cooperations and leadership in material science. He emphasized the importance of inelastic scattering. The value of neutrons lies in that neutrons go through the heart of elementary excitation region of most of
the important materials in energy-momentum dispersion relation. Among the various frontiers exemplified by him, I might note here: dynamical process in DNA printing and dynamical process in antigen-antibody interactions. Dr. M. Izumi, JAERI, gave us an excellent introductory overview where he touched on the substitution of hydrogen by deuterium, the backscattering spectrometer, the time-of-flight quasielastic scattering spectrometer, the polarized neutron beam, neutron spin-echo spectrometer, and so on.

Dr. G. Shirane, Brookhaven National Laboratory, clearly showed the new development in elucidation of the microscopic mechanism in structural phase transitions by recent detailed neutron scattering experiments. Prof. Y. Endoh, Tohoku University, showed the great importance of neutron scattering experiments in the study of magnetism with an example of La$_2$-$_x$Sr$_x$CuO$_4$. Dr. A.D. Taylor, ISIS Facility, Rutherford Appleton Laboratory, showed with beautiful viewgraphs that the dynamic range of wave vector and the energy of neutron scattering experiments has been remarkably widened in very diverse fields of research with pulsed neutron sources. Dr. Y. Morii, JAERI, showed the practical use of neutron scattering experiments with various methods of elastic scattering, inelastic scattering, small angle scattering and so on to study fundamental properties of materials such as shape memory alloy.

Dr. D. Richter, IFF, Jülich, made research on structural variation of one-dimensional polymer chains and star polymers by small angle neutron scattering, and also on molecular dynamics by spin-echo method. He assumed a tube model concerning self-diffusion of polymer chains in polymer melt system. Prof. T. Hashimoto, Kyoto University, discussed space-time organization of structure in polymer blends ordering process via spinodal decomposition, observing global, boundary and local structures by small angle neutron scattering and light scattering. Dr. H. Ohno, JAERI, made a presentation of neutron diffraction work on three-dimensional structure of random systems such as glassy state of PbO-SiO$_2$ system, liquid metals and molten salts for nuclear applications. The utilization of isotopic substitution samples was pointed out. He also emphasized the usefulness of molecular dynamics computer simulation. And, he made a short introduction of the 8 GeV synchrotron radiation facility, SPring-8, which is under construction as a joint work of JAERI and Riken, since he is an important member of the joint team of SPring-8. The SPring-8 is scheduled for completion in 1998, which is three years later than the centennial of the discovery of X-ray in 1895. Dr. G. Zaccâé, Institut de Biologie Structurale and Institut Laue-Langevin, discussed research on the
structures, interactions and dynamics of biological molecules by neutron
diffraction, and elastic and inelastic neutron scattering experiments with
deuterium labelling of samples and with various energy resolutions of about 1
µeV at the minimum. He also urged making single crystals of larger than 1 mm³
for biological study.

Prof. H.Rauch, Atominstitut der Österreichischen Universitäten, who is
the inventor of a perfect crystal interferometer, showed us many beautiful
quantum mechanical measurements with neutron interferometry. Among them,
a detection of extremely small energy loss of 10⁻¹⁷eV was especially impressive
to me. Splendid electron holographical work by Dr. A.Tonomura, Advanced
Research Laboratory, Hitachi Ltd., was very stimulating to many neutron
spectroscopists, too, I am sure. Prof. M.Utsuro, Kyoto University, made a
presentation of the studies with ultra-cold neutrons by view-graphs with "Alice
in Wonderland", which gave us pleasant expectations of future development. I
have been informed by the JAERI staff that instrumentation of this type is going
on at JRR-3M. Neutron bottle, neutron mirror, etc. remind me of an impressive
lecture by Prof. H.Maier-Leibnitz at Oak Ridge National Laboratory when I
was there in 1962 or '63, which was about the very inventive utilization of a
research reactor at Garching including a neutron guide tube. After that time,
the slowing down of neutrons by gravity, neutron bottles, etc. were rather
natural topics among some neutron physicists, but had not been realized for
many years. I personally was very much impressed that many dreams had been
realized.

Dr. J.P.Barton, NRE Inc., showed us some quite worthwhile development
of the neutron radiography, including computed tomography. Dr. R.E.Jervis,
University of Toronto, showed us broad uses of reactor neutrons for studying
the microcomposition of materials, typically lunar rocks, environmental samples
and so on. The data on ashes from hospital incinerators and on the contents of
heavy elements in commercial plastics was remarkable. I hope this kind of work
promotes a fair understanding of environmental problem by the public, but a
detection of negligible amounts of toxic materials by the high sensitivity of
advanced technology does not necessarily indicate environmental worry. I say
this since low level radiations of the order of local fluctuation of natural
background frequently become issues superfluously with agitation by so-called
environmentalists sometimes.
Next, in the program we scheduled to have a topical invited talk by Prof. H. Hatanaka, Teikyo University, on "Boron-Neutron Capture Therapy for Incurable Cancer and Inoperable Brain Tumors" for the first talk in yesterday's evening session. But, unfortunately, Prof. Hatanaka was hospitalized just after he arrived at the hotel in Mito the night before yesterday. We sincerely hope for his quick recovery.

Dr. G. H. Lander, CEC Joint Research Center, seemed to use the word "gloomy picture" for the present and near future situation of neutron source facilities, but we have had some encouragement since there are at least the plans for the Advanced Neutron Source at ORNL, European Spallation Source of 5-MW incident beam power, and so on. In this context, I might tell you that JAERI has a plan to develop an intense proton linac for the incineration of transuranium nuclides in high level nuclear wastes as the first purpose, and this facility may also provide an intense neutron source for various fundamental researches. Dr. Lander also pointed out the necessity of publicity. I would like to return to this point later.

Now, because of the time limit, allow me to stop referring to each speaker and not to comment on today's sessions, and also not to comment on the Poster Sessions which contain about 130 papers. But, I would like to comment on a more general view. Most researches using neutrons have more or less enjoyed the benefits of the whole nuclear energy development. Nuclear energy development consists of extremely wide disciplines, hence it promotes many kinds of small sciences, too. We believe that nuclear energy is the best major energy source from many points of view including the global environmental viewpoint, however, the world nuclear energy community suffers from a public acceptance difficulty, and nuclear energy research and development investment is unfortunately declining worldwide. We must reverse this tendency by all means. Basic research scientists may also contribute to publicity for proper knowledge of nuclear energy. If we finally fail to achieve the public acceptance of the peaceful uses of nuclear energy, however useful it may be for a majority, we might also fail in future to achieve any new large scale technological system which is difficult to evaluate without expert knowledge.

Finally, I wish you a prosperous future in research and development with neutrons. Thank you for your attention.
<table>
<thead>
<tr>
<th>Authors</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abe, H.</td>
<td>P - 123</td>
</tr>
<tr>
<td>Achiwa, N.</td>
<td>P - 151, 304</td>
</tr>
<tr>
<td>Aizawa, K.</td>
<td>P - 213, 302, 306, 511</td>
</tr>
<tr>
<td>Ajiro, Y.</td>
<td>P - 124, 125</td>
</tr>
<tr>
<td>Akiba, E.</td>
<td>P - 104, 117</td>
</tr>
<tr>
<td>Akimitsu, J.</td>
<td>P - 110, 111</td>
</tr>
<tr>
<td>Akine, Y.</td>
<td>P - 503</td>
</tr>
<tr>
<td>Aldyoshi, T.</td>
<td>P - 304</td>
</tr>
<tr>
<td>Andow, T.</td>
<td>P - 136</td>
</tr>
<tr>
<td>Arai, M.</td>
<td>P - 103, 113, 138, 157</td>
</tr>
<tr>
<td>Asano, H.</td>
<td>P - 210, 508</td>
</tr>
<tr>
<td>Asano, T.</td>
<td>P - 101, 124</td>
</tr>
<tr>
<td>Ataka, M.</td>
<td>P - 209</td>
</tr>
<tr>
<td>Atake, T.</td>
<td>P - 129</td>
</tr>
<tr>
<td>Barton, J.P.</td>
<td>I - 16</td>
</tr>
<tr>
<td>Bekui, T.</td>
<td>P - 138</td>
</tr>
<tr>
<td>Boldeman, J.</td>
<td>P - 611</td>
</tr>
<tr>
<td>Brunier, T.M.</td>
<td>P - 203</td>
</tr>
<tr>
<td>Child, H.R.</td>
<td>P - 146, 157</td>
</tr>
<tr>
<td>Chou, H.</td>
<td>P - 146</td>
</tr>
<tr>
<td>Churei, H.</td>
<td>P - 503</td>
</tr>
<tr>
<td>Clausen, K.N.</td>
<td>P - 116</td>
</tr>
<tr>
<td>Cookson, D.</td>
<td>P - 611</td>
</tr>
<tr>
<td>Date, M.</td>
<td>I - 1</td>
</tr>
<tr>
<td>David, W.I.F.</td>
<td>P - 210</td>
</tr>
<tr>
<td>Davis, R.L.</td>
<td>P - 611</td>
</tr>
<tr>
<td>Donni, A.</td>
<td>P - 119, 121</td>
</tr>
<tr>
<td>Ebisawa, T.</td>
<td>P - 302, 304, 602</td>
</tr>
<tr>
<td>Eguchi, M.</td>
<td>P - 412</td>
</tr>
<tr>
<td>Elconine, M.M.</td>
<td>P - 611</td>
</tr>
<tr>
<td>Enderle, M.</td>
<td>P - 116</td>
</tr>
<tr>
<td>Endo, T.</td>
<td>P - 513</td>
</tr>
<tr>
<td>Endoh, Y.</td>
<td>I - 6, P - 103, 113, 118, 119, 128</td>
</tr>
<tr>
<td></td>
<td>140, 157</td>
</tr>
<tr>
<td>Fernandez-Baca, J.A.</td>
<td>P - 155</td>
</tr>
<tr>
<td>Fischer, P.</td>
<td>P - 121</td>
</tr>
<tr>
<td>Fruchart, D.</td>
<td>P - 117</td>
</tr>
<tr>
<td>Fujishita, K.</td>
<td>P - 146, 224</td>
</tr>
<tr>
<td>Fujiy, H.</td>
<td>P - 139</td>
</tr>
<tr>
<td>Fujii, T.</td>
<td>P - 407</td>
</tr>
<tr>
<td>Fujii, Y.</td>
<td>I - 19, P - 504</td>
</tr>
<tr>
<td>Fujikawa, S.I.</td>
<td>P - 214</td>
</tr>
<tr>
<td>Fujime, S.</td>
<td>P - 402, 405</td>
</tr>
<tr>
<td>Fujisaki, H.</td>
<td>P - 142</td>
</tr>
<tr>
<td>Fujinami, S.</td>
<td>P - 117</td>
</tr>
<tr>
<td>Fuketa, T.</td>
<td>Summary Talk</td>
</tr>
<tr>
<td>Fukuda, K.</td>
<td>P - 156</td>
</tr>
<tr>
<td>Funahashi, H.</td>
<td>P - 32</td>
</tr>
<tr>
<td>Funahashi, S.</td>
<td>P - 104, 109, 111, 112, 115, 136</td>
</tr>
<tr>
<td></td>
<td>141, 142, 143, 144, 146, 147, 150</td>
</tr>
<tr>
<td></td>
<td>154, 155, 156, 158, 202, 216, 224</td>
</tr>
<tr>
<td></td>
<td>226, 252</td>
</tr>
<tr>
<td>Furrer, A.</td>
<td>P - 121</td>
</tr>
<tr>
<td>Furrusaka, M.</td>
<td>P - 214</td>
</tr>
<tr>
<td>Haga, Y.</td>
<td>P - 102, 148</td>
</tr>
<tr>
<td>Hajiwood, A.K.</td>
<td>P - 44</td>
</tr>
<tr>
<td>Hamaguchi, Y.</td>
<td>P - 112, 226</td>
</tr>
<tr>
<td>Han, C.C.</td>
<td>I - 10, P - 205, 206, 217, 218, 222</td>
</tr>
<tr>
<td>Hannon, A.C.</td>
<td>P - 103, 203</td>
</tr>
<tr>
<td>Hasegawa, H.</td>
<td>I - 10, P - 205, 221, 222</td>
</tr>
<tr>
<td>Hasegawa, Y.</td>
<td>P - 305</td>
</tr>
<tr>
<td>Hashiguchi, R.R.</td>
<td>Short Note</td>
</tr>
<tr>
<td>Hashimoto, M.</td>
<td>P - 302</td>
</tr>
<tr>
<td>Hashimoto, T.</td>
<td>P - 10, P - 205, 221, 222</td>
</tr>
<tr>
<td>Hatanaka, H.</td>
<td>I - 4, P - 506, 507</td>
</tr>
<tr>
<td>Hayakawa, H.</td>
<td>P - 117</td>
</tr>
<tr>
<td>Hayashi, M.</td>
<td>P - 512</td>
</tr>
<tr>
<td>Hayter, J.B.</td>
<td>I - 21</td>
</tr>
<tr>
<td>Hibi, T.</td>
<td>P - 405</td>
</tr>
<tr>
<td>Hidaka, M.</td>
<td>P - 607</td>
</tr>
<tr>
<td>Hidaka, Y.</td>
<td>P - 103</td>
</tr>
<tr>
<td>Hino, M.</td>
<td>P - 394</td>
</tr>
<tr>
<td>Hiraga, K.</td>
<td>P - 109, 144</td>
</tr>
<tr>
<td>Hirai, T.</td>
<td>P - 109</td>
</tr>
<tr>
<td>Hirota, J.</td>
<td>P - 510</td>
</tr>
<tr>
<td>Hoek, M.</td>
<td>P - 609</td>
</tr>
<tr>
<td>Honda, M.</td>
<td>P - 409, 410, 414</td>
</tr>
<tr>
<td>Honda, Y.</td>
<td>P - 610</td>
</tr>
<tr>
<td>Hoshino, S.</td>
<td>P - 123</td>
</tr>
<tr>
<td>Hosoya, S.</td>
<td>P - 103, 113, 140</td>
</tr>
<tr>
<td>Howard, C.J.</td>
<td>P - 131, 611</td>
</tr>
<tr>
<td>Huang, J.</td>
<td>P - 127</td>
</tr>
<tr>
<td>Hutchings, M.</td>
<td>I - 18</td>
</tr>
<tr>
<td>Ibberson, R.M.</td>
<td>P - 210</td>
</tr>
<tr>
<td>Ichikawa, H.</td>
<td>P - 509, 608</td>
</tr>
<tr>
<td>Ichikawa, K.</td>
<td>P - 215</td>
</tr>
<tr>
<td>Idemitsu, K.</td>
<td>P - 513</td>
</tr>
<tr>
<td>Iguchi, T.</td>
<td>P - 406</td>
</tr>
<tr>
<td>Iijima, K.</td>
<td>P - 511</td>
</tr>
<tr>
<td>Iizuka, K.</td>
<td>P - 42</td>
</tr>
<tr>
<td>Iizumi, M.</td>
<td>I - 2</td>
</tr>
<tr>
<td>Ikeda, S.</td>
<td>P - 128, 145, 148, 149</td>
</tr>
<tr>
<td>Ikeda, H.</td>
<td>P - 130</td>
</tr>
<tr>
<td>Inami, T.</td>
<td>P - 116, 137</td>
</tr>
<tr>
<td>Inui, M.</td>
<td>P - 219, 220, 502</td>
</tr>
<tr>
<td>Iriyama, T.</td>
<td>P - 144</td>
</tr>
<tr>
<td>Ishigaki, T.</td>
<td>P - 112</td>
</tr>
<tr>
<td>Ishii, Y.</td>
<td>P - 156, 158, 159</td>
</tr>
<tr>
<td>Ishikawa, K.</td>
<td>P - 606</td>
</tr>
<tr>
<td>Name</td>
<td>Page</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>Ishiwata, M.</td>
<td>P-512</td>
</tr>
<tr>
<td>Ito, A.</td>
<td>P-105</td>
</tr>
<tr>
<td>Ito, Y.</td>
<td>P-202,223,409,410,414</td>
</tr>
<tr>
<td>Itoh, S. (Tohoku)</td>
<td>P-116</td>
</tr>
<tr>
<td>Itoh, S. (KEK)</td>
<td>P-118</td>
</tr>
<tr>
<td>Iversen, B.B.</td>
<td>P-133</td>
</tr>
<tr>
<td>Ivana, H.</td>
<td>P-406</td>
</tr>
<tr>
<td>Izumi, F.</td>
<td>P-104,129</td>
</tr>
<tr>
<td>Izumi, Y.</td>
<td>P-216</td>
</tr>
<tr>
<td>Kiyanagi, Y.</td>
<td>P-406</td>
</tr>
<tr>
<td>Knoe, R.</td>
<td>P-611</td>
</tr>
<tr>
<td>Kobayashi, H. (Elec.)</td>
<td>P-136</td>
</tr>
<tr>
<td>Kobayashi, H. (Hiro)</td>
<td>P-622</td>
</tr>
<tr>
<td>Kobayashi, H. (Rikkyo)</td>
<td>P-411,413,504</td>
</tr>
<tr>
<td>Kobayashi, K.</td>
<td>P-144</td>
</tr>
<tr>
<td>Kobayashi, N.</td>
<td>P-108</td>
</tr>
<tr>
<td>Kobayashi, T. (KURRI)</td>
<td>P-501,506</td>
</tr>
<tr>
<td>Kodaira, T.</td>
<td>P-608</td>
</tr>
<tr>
<td>Koga, T.</td>
<td>P-201</td>
</tr>
<tr>
<td>Kohgi, M.</td>
<td>P-102,120,121,139,141,148</td>
</tr>
<tr>
<td>Kohn, K.</td>
<td>152,153</td>
</tr>
<tr>
<td>Koike, Y.</td>
<td>P-115</td>
</tr>
<tr>
<td>Koizumi, S.</td>
<td>P-108</td>
</tr>
<tr>
<td>Kojima, H.</td>
<td>P-221</td>
</tr>
<tr>
<td>Komatsu, H.</td>
<td>P-113</td>
</tr>
<tr>
<td>Komatsu, H. (Tsunuba)</td>
<td>P-377</td>
</tr>
<tr>
<td>Komatsubara, T.</td>
<td>P-119</td>
</tr>
<tr>
<td>Komura, S.</td>
<td>P-222,261,602</td>
</tr>
<tr>
<td>Konishi, A.</td>
<td>P-146</td>
</tr>
<tr>
<td>Kosaki, K.</td>
<td>P-304</td>
</tr>
<tr>
<td>Kotani, S.</td>
<td>P-215</td>
</tr>
<tr>
<td>Koyama, Y.</td>
<td>P-610</td>
</tr>
<tr>
<td>Kubota, S.</td>
<td>P-166</td>
</tr>
<tr>
<td>Kula, J.</td>
<td>P-129</td>
</tr>
<tr>
<td>Kumazawa, S.</td>
<td>P-121,133</td>
</tr>
<tr>
<td>Kunitomi, N.</td>
<td>P-135</td>
</tr>
<tr>
<td>Kuriyama, H.</td>
<td>P-101,124</td>
</tr>
<tr>
<td>Kuroiwa, Y. (Tohoku)</td>
<td>P-129</td>
</tr>
<tr>
<td>Kuroiwa, Y. (Chiba)</td>
<td>P-146,506</td>
</tr>
<tr>
<td>Lander, G.H.</td>
<td>I-3</td>
</tr>
<tr>
<td>Larsen, F.K.</td>
<td>P-149</td>
</tr>
<tr>
<td>Larsen, F.K.</td>
<td>P-133</td>
</tr>
<tr>
<td>Lebech, B.</td>
<td>P-151</td>
</tr>
<tr>
<td>Magara, M.</td>
<td>P-414</td>
</tr>
<tr>
<td>Makita, T.</td>
<td>P-150,154</td>
</tr>
<tr>
<td>Maruyama, K.</td>
<td>P-502</td>
</tr>
<tr>
<td>Matsuoka, M.</td>
<td>P-122</td>
</tr>
<tr>
<td>Matsuoka, Y. (Tohoku)</td>
<td>P-401,404,405,505</td>
</tr>
<tr>
<td>Masumoto, C.</td>
<td>P-46</td>
</tr>
<tr>
<td>Masumoto, H.</td>
<td>P-111</td>
</tr>
<tr>
<td>Masumoto, K.</td>
<td>P-506,507</td>
</tr>
<tr>
<td>Masumoto, S.</td>
<td>P-411</td>
</tr>
<tr>
<td>Matsuo, T.</td>
<td>P-506</td>
</tr>
<tr>
<td>Matsushita, Y.</td>
<td>P-277,278</td>
</tr>
<tr>
<td>Mekata, M.</td>
<td>P-101,124</td>
</tr>
<tr>
<td>Mezei, F.</td>
<td>22</td>
</tr>
<tr>
<td>Mihara, K.</td>
<td>P-288</td>
</tr>
<tr>
<td>Mikii, H.</td>
<td>P-147</td>
</tr>
<tr>
<td>Mine, Y.</td>
<td>P-108,111</td>
</tr>
<tr>
<td>Minezaki, Y.</td>
<td>P-209</td>
</tr>
</tbody>
</table>
Mino, M.
Minobe, M.
Minobe, T.
Miraglia, S.
Mishima, K.
Mishima, Y.
Mika, K.
Mitsuda, S.
Mitsuji, T.
Miyazaki, Y.
Mizobuchi, D.
Mizuki, J.
Mizuseki, H.
Mogi, Y.
Moon, R.M.
Mori, K.
Mori, N.
Morii, Y.
Morisako, T.
Morishima, N.
Mortensen, K.
Moss, S.C.
Motoyama, M.
Motoya, K.
Murakami, S.
Murayama, C.

Ohara, K.
Ohashi, M.
Ohishi, Y.
Ohtkubo, K.
Ohtkubo, M.
Ohno, H.
Ohnuma, M.
Ohyama, K.
Ohashi, K.
Obotomo, S.
Okamura, K.
Okayama, Y.
Okumura, K.
Omata, T.
Ono, A.
Ono, K.
Ono, T.
Oxera-Yamamura, N.
Onodera, A.
Onodera, H.
Onuki, Y.
Oohara, Y.
Oomi, G.
Oskabe, T.
Otomo, T.
Oyamada, A.
Ozaki, Y.

\(N\)
Nagai, M.
Nagashima, A.
Nakazawa, Y. (Tobata)
Nakazawa, Y. (Kagawa)
Nakai, Y. (Shizuoka)
Nakai, Y. (Tsukuba)
Nakajima, K.
Nakamura, H. (Kyoto)
Nakamura, H. (Tobata)
Nakamura, Y.
Nakanishi, T. M.
Nakazawa, M.
Nakazawa, T.
Nemoto, D.
Nemoto, H.
Niedow, R. M.
Niimura, N.
Nishi, M.
Nishihara, H.
Nishitani, T.
Noda, I.
Noda, Y.
Noji, T.
Nomura, M.

\(P\)
Penfold, J.
Pontournier, L.
Pringle, O. A.
Purwanto, S.

\(R\)
Ranck, H.
Richardson, J. W.
Richter, D.

\(S\)
Saegusa, Y.
Saito, Y.
Sakai, K.
Sakata, M.
Sakuma, Y.
Sasaki, M.
Sasaki, T.
Sato, M.
Sato, N.
Sato, T.
Sato, T.
Sawahata, H.
Schwanh, D.
Scicluna, F. D.
Sekiguchi, M.
Seko, H.
Serizawa, H.

\(O\)
Oda, M.
Oda, Y.

Page P-138
Page P-224
Page P-507
Page P-117
Page P-405
Page P-510
Page P-208
Page P-101, 102, 124
Page P-408
Page P-109
Page P-604
Page P-128
Page P-225
Page P-217, 218
Page P-135
Page P-112
Page P-102, 148, 155
Page I-8, P-104, 108, 109, 141, 142, 143
Page 144, 150, 154, 158
Page P-607
Page P-604
Page P-202
Page P-146
Page P-137, 138
Page P-106
Page P-508
Page P-155
Page P-403
Page P-136, 143, 603
Page P-224
Page P-401
Page P-305
Page I-11, P-154, 158
Page P-228
Page P-139, 147, 152
Page P-123
Page P-405
Page P-223
Page P-102
Page P-303
Page P-113, 140
Page P-407
Page P-501
Page P-138
Page P-210
Page P-135, 151
Page P-136, 143
Page P-120, 121, 122, 124
Page P-65
Page P-102, 120, 139, 141, 148, 152, 153
Page P-152
Page P-152
Page P-132
Page P-20
Page P-117
Page P-135
Page P-143
Page I-13
Page P-126
Page I-9
Page P-501
Page P-105
Page P-501
Page P-131, 133
Page P-505
Page P-510
Page P-148
Page P-142
Page P-119, 120
Page P-131
Page P-503
Page P-505
Page P-514
Page P-502
Page P-203
Page P-504
Page P-501
Page P-156
<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yasuda, H.</td>
<td>P-128</td>
</tr>
<tr>
<td>Yasunishi, A.</td>
<td>P-411</td>
</tr>
<tr>
<td>Yazaki, A.</td>
<td>P-130</td>
</tr>
<tr>
<td>Yokoi, E.</td>
<td>P-202,602</td>
</tr>
<tr>
<td>Yoneda, K.</td>
<td>P-402,405</td>
</tr>
<tr>
<td>Yonezawa, C.</td>
<td>P-408,410,414</td>
</tr>
<tr>
<td>Yonezu, I.</td>
<td>P-117</td>
</tr>
<tr>
<td>Yoshinari, A.</td>
<td>P-511</td>
</tr>
<tr>
<td>Yoshizawa, H.</td>
<td>P-101,102,105,122,124</td>
</tr>
<tr>
<td>Yoshizawa, Y.</td>
<td>P-141</td>
</tr>
</tbody>
</table>

**Z**

<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zaccai, C.</td>
<td>I-12</td>
</tr>
<tr>
<td>Zhang, Z.H.</td>
<td>P-501</td>
</tr>
</tbody>
</table>
Proceedings of the Fifth International Symposium on Advanced Nuclear Energy Research

—Neutrons as Microscopic Probes—

March 10—12, 1993, Joyo Geibun Center, Mito, Ibaraki, Japan

Organized and Sponsored by
Japan Atomic Energy Research Institute

in Cooperation with
ATOMIC ENERGY SOCIETY OF JAPAN
THE PHYSICAL SOCIETY OF JAPAN
THE JAPAN INSTITUTE OF METALS
THE CRYSTALLOGRAPHIC SOCIETY OF JAPAN
THE JAPAN SOCIETY OF APPLIED PHYSICS
THE SOCIETY OF POLYMERIC SCIENCE, JAPAN

日本原子力研究所
Japan Atomic Energy Research Institute
JAERI-Mレポートは、日本原子力研究所が不定期に公刊している研究報告書です。
入手の際は、日本原子力研究所技術情報部情報資料課（〒319-11 茨城県つくば市東海村）にて、お申しこみください。なお、このほかに財団法人原子力広報会資料センター（〒319-11 茨城県つくば市東海村日本原子力研究所内）で複写による実費購入をおこなっております。

JAERI-M reports are issued irregularly.
Inquiries about availability of the reports should be addressed to Information Division, Department of Technical Information, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-11, Japan.

© Japan Atomic Energy Research Institute, 1993
Published by JAERI, November 1993
Proceedings of the Fifth International Symposium on Advanced Nuclear Energy Research

— Neutrons as Microscopic Probes —

March 10~12, 1993, Joyo Geibun Center, Mito, Ibaraki, Japan

Organized and Sponsored by
Japan Atomic Energy Research Institute

in Cooperation with
ATOMIC ENERGY SOCIETY OF JAPAN
THE PHYSICAL SOCIETY OF JAPAN
THE JAPAN INSTITUTE OF METALS
THE CRYSTALLOGRAPHIC SOCIETY OF JAPAN
THE JAPAN SOCIETY OF APPLIED PHYSICS
THE SOCIETY OF POLYMER SCIENCE, JAPAN
Organizing Committee

Chairman: Takumi ASAOKA (JAERI)

Members of Committee:
T. Akabane (NIRIM)
Y. Endoh (Tohoku Univ.)
Y. Hamaguchi (Muroran Inst. of Tech.)
M. Iizumi (JAERI)
K. Ishigure (Univ. of Tokyo)
K. Kaji (Kyoto Univ.)
K. Katsumata (RIKEN)
S. Kikuta (Univ. of Tokyo)
T. Kondoh (JAERI)
G. Matsumoto (Prof. emeritus, Nagoya Univ., Fujita Health Univ.)
M. Saitoh (JAERI)
E. Tachikawa (JAERI)
T. Tamazawa (JAERI)
Y. Yamada (Prof. emeritus, Osaka Univ.)
H. Yamaoka (Kyoto Univ.)
N. Watanabe (KEK)
K. Asai (JAERI)
Y. Fujii (Univ. of Tokyo)
T. Hiraoka (JAERI)
M. Izawa (JAIH)
M. Ishii (JAERI)
Y. Kaneko (JAERI)
W. Kawakami (JAERI)
S. Komura (Hiroshima Univ.)
S. Matsuru (JAERI)
H. Nakahara (Tokyo Metropolitan Univ.)
T. Noda (NIRIM)
E. Shirai (JAERI)
H. Takahashi (JAERI)
M. Utsuro (Kyoto Univ.)
Y. Yamaguchi (Tohoku Univ.)
T. Yanagisawa (PNC)

Secretary:
S. Funahashi (JAERI)
Y. Mitadera (JAERI)
T. Takahashi (JAERI)

T. Kodaira (JAERI)
T. Numata (JAERI)

Secretariat of the Symposium:
Eiji Shirai
Department of Research Reactor
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319–11, Japan
Phone 0292-82-5318
Fax 0292-82-5258

Editorial Working Group
Leader: H. Takahashi

Members of Working Group:
N. Hiramatsu, M. Hoshi, H. Tornimitsu, H. Shitomi,
H. Ichikawa, K. Okumura, K. Yokoo
# CONTENTS

<table>
<thead>
<tr>
<th>Opening Address</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.Shimomura (President, JAERI)</td>
<td>1</td>
</tr>
</tbody>
</table>

## Keynote Lectures

<table>
<thead>
<tr>
<th>I-1</th>
<th>Expectations for Neutrons as Microscopic Probes</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M.Date (Osaka Univ.)</td>
<td></td>
</tr>
<tr>
<td>I-2</td>
<td>Neutrons as a Probe — An Overview —</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>M.Iizumi (JAERI)</td>
<td></td>
</tr>
</tbody>
</table>

## Special Invited Talk

<table>
<thead>
<tr>
<th>I-3</th>
<th>Prospect for Neutron Probes in the 21st Century</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G.H.Lander (EITU, Germany)</td>
<td></td>
</tr>
</tbody>
</table>

## Topical Invited Talk

<table>
<thead>
<tr>
<th>I-4</th>
<th>Boron-Neutron Capture Therapy for Incurable Cancer and Inoperable Brain Tumors</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H.Hatanaka (Teikyo Univ.)</td>
<td></td>
</tr>
</tbody>
</table>

## Session I : Development of Solid State Physics with Neutron Probes

<table>
<thead>
<tr>
<th>I-5</th>
<th>Phase Transitions and Neutron Scattering</th>
<th>29</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G.Shirane (BNL, USA)</td>
<td></td>
</tr>
<tr>
<td>I-6</td>
<td>Recent Development in Magnetic Neutron Scattering Studies</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Y.Endoh (Tohoku Univ.)</td>
<td></td>
</tr>
<tr>
<td>I-7</td>
<td>Expanding the Frontiers of Neutron Scattering</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>A.D.Taylor (RAL, UK)</td>
<td></td>
</tr>
<tr>
<td>I-8</td>
<td>Alloys Studied by Neutron Scattering</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Y.Morii (JAERI)</td>
<td></td>
</tr>
</tbody>
</table>

**A Short Note on Early Observations of Neutron Scattering by Crystals**

R.R.Hashiguchi (Univ. of Tokyo Prof. of Emeritus) 60

## Session II : Complex Structure Study with Neutron Probes

<table>
<thead>
<tr>
<th>I-9</th>
<th>Polymer Research by Neutron Scattering</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D.Richter (KFA, Germany)</td>
<td></td>
</tr>
<tr>
<td>I-10</td>
<td>SANS Studies of Space-time Organization of Structure in Polymer Blends</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>T.Hashimoto, H.Jinnai, H.Hasegawa (Kyoto Univ.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C.C.Han (NIST, USA)</td>
<td></td>
</tr>
<tr>
<td>I-11</td>
<td>Neutron Diffraction on Random Systems</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>H.Ohno (JAERI)</td>
<td></td>
</tr>
</tbody>
</table>
I-12 Biology with Neutrons
G. Zaccar (ILL, France)

Session II: Fundamental Physics Research with Neutron Beam
I-13 Fundamental Research with Neutron Interferometry
H. Rauch (Austria Univ., Austria)
I-14 Expectations for Neutron Experiments
- An Electron Physicist's View -
A. Tonomura (Hitachi Ltd.)
I-15 Fundamental Physics with Ultracold Neutrons
M. Utsuro (KURRI)

Session IV: Non-scattering Research with Neutron Probes
I-16 Neutron Radiography — Status and International Prospects
J.P. Barton (NRE Inc., USA)
I-17 Uses of Reactor Neutrons for Studying the Microcomposition
of Materials
R.E. Jervis (Univ. of Toronto, Canada)

Session V: Novel Application of Neutron Beam
I-18 Commercial Applications of Neutron Scattering
M.T. Hutchings (Harwell Lab., UK)
I-19 Complementary Applications of Scattering by Neutrons and SRX-rays
Y. Fujii (Univ. of Tokyo)
I-20 Neutron Reflectometry
A.D. Taylor, J. Penfold (RAL, UK)

Session VI: Technical Innovation of Neutron Beam Experiment
I-21 New Techniques in Neutron Scattering
J.B. Hayter (ORNL, USA)
I-22 Applications of Polarized Neutrons
F. Mezei (HMI, Germany)

Panel Discussion: Future Research with Neutrons
- from JRR-3M to Next Generation Neutron Sources -
Chairman: Y. Yamada (Osaka Univ. Prof. Emeritus)

Summary Talk
T. Fuketa (JAERI)

Authors Index
### Poster Session

#### Session 1: Development of Solid State Physics with Neutron Probes

<table>
<thead>
<tr>
<th>Code</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-101</td>
<td>Neutron Diffraction Study in AgCrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Y.Oohara, H.Yoshizawa (Univ. of Tokyo)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S.Mitsuda (Science Univ. of Tokyo)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N.Yaguchi, H.Kuriyama, T.Asano, M.Mekata (Fukui Univ.)</td>
</tr>
<tr>
<td>P-102</td>
<td>Crystal Field Splitting in CeAs and CeP under High Pressure</td>
<td>Y.Oohara, Y.Okayama, H.Takahashi, H.Yoshizawa, N.Mori (Univ. of Tokyo)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S.Mitsuda (Science Univ. of Tokyo)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T.Osakabe, Y.Haga, M.Kohgi, T.Suzuki (Tohoku Univ.)</td>
</tr>
<tr>
<td>P-103</td>
<td>Lattice Instability of High-Te Oxide Superconductors Studied</td>
<td>M.Arai (kobe Univ.)</td>
</tr>
<tr>
<td></td>
<td>by Inelastic Neutron Scattering</td>
<td>K.Yamada, Y.Endoh, S.Hosoya (Tohoku Univ.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y.Hidaka (NTT)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.C.Hannon, A.D.Taylor (RAL, UK)</td>
</tr>
<tr>
<td>P-104</td>
<td>Structural Phase Transitions of NaV&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;11&lt;/sub&gt; and SrV&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;11&lt;/sub&gt;</td>
<td>Y.Kanke, F.Izumi, K.Kato (NIRIM)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E.Akiha (Natl. Chem. Lab. for Industry)</td>
</tr>
<tr>
<td>P-105</td>
<td>Neutron Scattering Study of Heisenberg-like Spin Glass Ni&lt;sub&gt;1-x&lt;/sub&gt;Mn&lt;sub&gt;x&lt;/sub&gt;TiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H.Kawano, H.Yoshizawa (Univ. of Tokyo)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A.Ito (Ochanomizu Univ.)</td>
</tr>
<tr>
<td>P-106</td>
<td>Spin Dynamics of Concentrated Metallic Spin Glasses</td>
<td>K.Motoya, S.Kubota (Saitama Univ.)</td>
</tr>
<tr>
<td>P-107</td>
<td>On the 100 Magnetic Diffuse Peak in Fe Precipitates in Cu</td>
<td>Y.Tsunoda (Osaka Univ.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R.M.Nicklow (ORNL, USA)</td>
</tr>
<tr>
<td>P-108</td>
<td>Site Preference, Superconductivity and Magnetism in</td>
<td>Y.Koike, M.Kaiwa, M.Kato, H.Sunagawa, T.Noji, Y.Saito,</td>
</tr>
<tr>
<td></td>
<td>Pb&lt;sub&gt;2&lt;/sub&gt;Sr&lt;sub&gt;Y&lt;/sub&gt;Ca(Cu&lt;sub&gt;1-x&lt;/sub&gt;M)&lt;sub&gt;x&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;(M=Fe,Co,Ni,Zn,Ga)</td>
<td>T.Kajitani, N.Kobayashi (Tohoku Univ.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
<tr>
<td>P-109</td>
<td>Crystal Structures of New Cuprates Containing CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Y.Miyazaki, H.Yamane, T.Kajitani, K.Hiraga, T.Hirai (Tohoku Univ.)</td>
</tr>
<tr>
<td></td>
<td>Analyzed by the Rietveld Method of Neutron Powder Diffraction</td>
<td>Y.Morii, S.Funahashi (JAERI)</td>
</tr>
</tbody>
</table>
P-110  Polarization Analysis on Two-dimensional Antiferromagnet ErFe$_2$O$_4$  254
H.Kito, J.Akimitsu (Aoyama-Gakuin Univ.)
K.Siratori (Osaka Univ.)
M.Nishi (Univ. of Tokyo)

P-111  Phonon Dispersion in Layered Structure ErFe$_2$O$_4$  260
H.Kito, J.Akimitsu (Aoyama-Gakuin Univ.)
S.Funahashi (JAERI)
K.Siratori (Osaka Univ.)

P-112  Crystal Structure and Superconductivity of LnBa$_2$Cu$_4$O$_8$
(Ln=Ho,Er,Y,Dy and Gd) Superconductors  261
T.Ishigaki, K.Mori, Y.Kawaguchi, Y.Hamaguchi (Murokan Inst. of Tech.)
S.Katano, S.Funahashi (JAERI)

P-113  Neutron Scattering Study on the Spin Dynamics of the Two
Dimensional Square Lattice Antiferromagnet, La$_2$NiO$_4$  269
K.Nakajima, K.Yamada, S.Hosoya, Y.Endoh, T.Omata (Tohoku Univ.)
M.Arai (Kobe Univ.)
A.D.Taylor (RAL, UK)

P-114  Polarized Neutron Scattering Study of $\beta$-Mn  277
M.Shiga, H.Nakamura (Kyoto Univ.)
M.Nishi, K.Kakurai (Univ. of Tokyo)

P-115  Neutron Diffraction Study and Magnetic Properties of La$_2$NiO$_4$.  284
N.Yamada (Univ. of Electro-communications)
N.Takada, K.Kohn (Waseda Univ.)
S.Funahashi (JAERI)

P-116  Neutron Scattering Experiments on Antiferromagnetic ABX$_4$ Systems:
Study of the Haldane Conjecture  292
K.Kakurai, T.Inami (Univ. of Tokyo)
K.Nakajima, S.Itoh (Tohoku Univ.)
H.Tanaka (Nagoya Univ.)
M.Enderle (Univ. of Mainz, Germany)
K.N.Clausen (RISO, Denmark)
M.Steiner (Hahn-Meitner-Institut, Germany)

P-117  Crystal Structure Refinement of Alloys and Hydrides of Zr(Mn$_{1-x}$M)$_x$
with M=V,Fe,Co,Ni and Al  300
S.Fujitani, I.Yonezu (Sanyo Electric Co. Ltd.)
D.Fruchart, J.L.Soubeyroux, L.Pontonnier, S.Miraglia (CNRS, France)

P-118  Neutron Depolarization Studies on Magnetic Flux in Superconductors  307
T.Watanabe, K.Yamada, Y.Endoh, N.Toyota (Tohoku Univ.)
S.Itoh (KEK)
H.Kojima, I.Tanaka (Yamanashi Univ.)
P-119 Magnetic Structure in Single Crystal of Antiferromagnetic Heavy Fermion Superconductor, UPd₂Al₃
H.Kita, A.Donni, Y.Endoh, N.Sato, T.Komatsubara (Tohoku Univ.)
K.Kakurai (Univ. of Tokyo)

308

P-120 Neutron Scattering Study of UX₃(X=Ga,Ge)
Y.Kuroiwa, M.Kohgi, T.Osakabe, N.Sato (Tohoku Univ.)
Y.Onuki (Univ. of Tsukuba)

314

P-121 Sample Dependence of Magnetic Ordering in the Ytterbium Monopnictides YbN and YbP
A.Donni, M.Kohgi, T.Suzuki (Tohoku Univ.)
L.Keller, P.Fischer, A.Furrer (ETH Zurich, Switzerland)

319

P-122 Soft Modes and Phase Transition at 74K in Rb₂ZnCl₄
H.Mashiyama, K.Sugimoto (Yamaguchi Univ.)
Y.Oohara, H.Yoshizawa (Univ. of Tokyo)

320

P-123 Structural Study in Metallic Sodium
H.Abe, K.Ohshima, T.Suzuki, S.Hoshino (Univ. of Tsukuba)
K.Kakurai (Univ. of Tokyo)

326

P-124 Magnetic Ordering in Delafossite-type Rhombohedral Antiferromagnets
M.Mekata, Y.Ajiro, N.Yaguchi, H.Kuriyama, T.Asano (Fukui Univ.)
H.Kadowaki, Y.Oohara, H.Yoshizawa (Univ. of Tokyo)
S.Mitsuda (Science Univ. of Tokyo)

327

P-125 Universality Classes of Magnetic Phase Transitions in the Stacked Triangular Lattice Antiferromagnets, CsMnBr₃ and CsMnI₃
Y.Ajiro (Fukui Univ.)
H.Kadowaki (Univ. of Tokyo)

335

P-126 Magnetic Structure of Fe₁₋ₓNbS₂
T.Suzuki (Univ. of Tsukuba)
S.Ikeda (KEK)
J.W.Richardson (ANL, USA)
Y.Yamaguchi (Tohoku Univ.)

343

P-127 Synthesis, Structure and Electrical Properties of the Thallium Ruthenate Pyrochlores
R.Kanno (Kobe Univ.)
J.Huang, A.W.Sleight (Oregon State Univ.)

347

P-128 Neutron Scattering Studies of Fe/Cr Multilayers
H.Yasuda, M.Takeda, Y.Endoh, K.Yamada, T.Watanabe (Tohoku Univ.)
A.Kamijo, J.Mizuk (NEC Corp.)

355
<table>
<thead>
<tr>
<th>Page</th>
<th>Title</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-129</td>
<td>Cu Ion Disordering in High Ionic Conductor Rh₄Cu₄I₄Cl₈</td>
<td>H.Kawaji, T.Atake (Tokyo Inst. of Tech.) R.Kanno (Kobe Univ.) P.Izumi (NIRIM) O.Yamamoto (Mie Univ.)</td>
</tr>
<tr>
<td>P-130</td>
<td>Determination of Paramagnetic $x(q,\omega)$ for a Metallic Antiferromagnet Mn₅Pt by TOF Method</td>
<td>Y.Todate (Ochanomizu Univ.) K.Tajima, A.Yazaki (Keto Univ.) S.Tomiyoshi (Ehime Univ.) H.Ikeda (KEK)</td>
</tr>
<tr>
<td>P-132</td>
<td>Phase Effect in 3-fold and 6-fold Potentials of CH₃ Group on Q-Dependence in Neutron Scattering</td>
<td>Y.Ozaki (Nagoya Inst. of Tech.)</td>
</tr>
<tr>
<td>P-133</td>
<td>Anharmonic Thermal Vibrations of Be Metal Found in the Mem Nuclear Density Map</td>
<td>M.Takata, M.Sakata (Nagoya Univ.) P.K.Larsen, B.B.Iversen (Aarhus Univ., Denmark) S.Kumazawa (Science Univ. of Tokyo)</td>
</tr>
<tr>
<td>P-134</td>
<td>Neutron Scattering Study of MnX₅ (X=Br,I)</td>
<td>T.Sato (Tokyo Inst. of Tech.) H.Kadowaki (Univ. of Tokyo)</td>
</tr>
<tr>
<td>P-135</td>
<td>Pressure Dependence of the Antiferromagnetic Ordering Temperature of Face-Centered-Cubic Iron</td>
<td>A.Onodera, Y.Tsunoda, N.Kunitomi (Osaka Univ.) O.A.Pringle, R.M.Nicklow, R.M.Moon (ORNL, USA)</td>
</tr>
<tr>
<td>P-136</td>
<td>Magnetic Order in the Competing Interaction State of Ternary Intermetallides DyMn₅Si₂ and DyMn₅Ge₂</td>
<td>M.Ohashi, H.Onodera, T.Ono, T.Andow, Y.Yamaguehi (Tohoku Univ.) S.Funahashi (JAERI) H.Kobayashi (Electrotechnical Lab.)</td>
</tr>
<tr>
<td>P-137</td>
<td>Magnetic Phase Transition of CsNiCl₃</td>
<td>K.Ubukata, M.Motokawa (Kobe Univ.) T.Inami, K.Kakurai (Univ. of Tokyo)</td>
</tr>
</tbody>
</table>
P-138 Magnetic Phase Transition of CsCuCl$_3$ in Pulsed Magnetic Field
M.Mino, K.Uhukata, T.Bokul, M.Arai, M.Motokawa (Kobe Univ.)
H.Tanaka (Nagoya Univ.) ........................................ 416

P-139 Dynamic Magnetic Response of a Gap-type Kondo Material CeNiSn
M.Kohgi, K.Ohyama, T.Osakabe, M.Kasaya (Tohoku Univ.)
T.Takahatake, H.Fujii (Hiroshima Univ.) .......................... 421

P-140 Magnetic Phase Diagram of Oxygen Nonstoichiometric La$_2$NiO$_4$ + $\delta$
T.Omata, K.Yamada, K.Nakajima, S.Hosoya, Y.Endoh (Tohoku Univ.) 426

P-141 Spin Wave Excitations in a Kondo Material CeCu$_3$
M.Kohgi, T.Osakabe (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI)
Y.Onuki (Univ. of Tsukuba)
H.Yoshizawa (Univ. of Tokyo) ........................................ 434

P-142 Powder Neutron Diffraction Study on Pb$_2$Sr$_2$YCu$_5$O$_{13}$ + $\delta$ ( $\delta$ = 0.0 and 1.67)
H.Fujishita (Kanazawa Univ.)
M.Sato (Nagoya Univ.)
Y.Morii, S.Funahashi (JAERI) ........................................ 439

P-143 Magnetic Order in Ternary Compounds ThMn$_5$Ge$_3$ and ThMn$_5$Sb
S.Purwanto, M.Ohashi, H.Onodera, H.Yamauchi, Y.Yamaguchi (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI) ........................................ 447

P-144 Neutron Powder Diffraction Study on Nd$_2$Fe$_{17}$N$_{10}$
with 0 $\leq$ x $\leq$ 3.0 and 0 $\leq$ y $\leq$ 1.0
T.Kajitani, H.Kato, Y.Nakagawa, K.Hiraga (Tohoku Univ.)
Y.Morii, S.Funahashi (JAERI)
T.Iriyama, K.Kobayashi (Asahi Chemical Industry Co. Ltd.) 455

P-145 Incoherent Neutron Scattering of Hydrogen Bond Compounds
I. Experiments at Steady Reactor
Y.Noda, I.Tamura (Chiba Univ.)
S.Ikeda (KEK)
Y.Yamada (Prof. of Emeritus, Osaka Univ.) ........................ 463

P-146 Structure of Martensitic Phase and Phonon Instability in Cu$_{53}$Zn$_{47}$
A.Konishi, Y.Kuroiwa, Y.Noda (Chiba Univ.)
K.Fuchizaki (Kyushu Univ.)
S.Funahashi, S.Katano (JAERI)
H.H Child (ORNL, USA)
H.Chou (BNL, USA)
Y.Yamada (Prof. of Emeritus, Osaka Univ.)
S.C.Moss (Univ. of Houston, USA) ................................. 468
P-147 Magnetic Structure of Itinerant Electron Antiferromagnets
Mn$_x$T$_{1-x}$Si (T=Cr,Fe) ........................................ 475
H.Miki, K.Ohoyama, Y.Yamaguchi (Tohoku Univ.)
S.Funahashi (JAERI)
S.Tomiyoishi (Ehime Univ.)

P-148 Crystal Field State and Magnetic Ordering of a Low Carrier System
CeP under High Pressure and Magnetic Field ................. 478
T.Osakabe, M.Kohgi, T.Suzuki, Y.Haga (Tohoku Univ.)
N.Mori, H.Takahashi (Univ. of Tokyo)
S.Ikeda (KEK)

P-149 Inelastic Neutron Scattering Measurements on Hydrogen-Involved
Molecular Libration in Superconducting x-(t$_4$-BEDT-TTF)$_2$Cu(NCS)$_2$ .. 479
S.Ikeda (KEK)

P-150 [110]TA$_5$ Phonon Dispersion Relations of BCC, B2 and
Heusler Phases in AuCuZn$_2$ Alloy ............................ 486
A.Nagasawa, R.Yamauchi (Nara Women's Univ.)
T.Makita, Y.Morii, S.Funahashi (JAERI)

P-151 High Pressure Neutron Diffraction Studies of
the Magnetic Structures of Tb,Ho and Er .................. 492
S.Kawano (KURRI)
N.Achiwa (Kyushu Univ.)
A.Onodera (Osaka Univ.)
Y.Nakai (Sizuoka Inst. of Sci. and Tech.)
B.Lebech (Riso, Denmark)

P-152 Neutron Quasi-elastic Scattering Study of Magnetic Fluctuations
in Yb Monopnictides ............................................. 500
K.Ohoyama, M.Kohgi, T.Otomo, T.Osakabe, A.Oyamada, T.Suzuki (Tohoku Univ.)

P-153 Neutron Scattering Study of Ce$_3$Au$_3$Sb$_4$ ................... 505
M.Kasaya, K.Kato, M.Kohgi, T.Osakabe (Tohoku Univ.)

P-154 Phonon Dispersion Anomaly in the Premartensitic
$\beta_1$-Phase Au-Zn Alloys .................................. 509
T.Makita, Y.Morii, S.Funahashi, H.Ohno (JAERI)
A.Nagasawa (Nara Women's Univ.)

P-155 Structural Phase Transition and Superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ .... 514
S.Katano, S.Funahashi (JAERI)
J.A.Fernandez-Baca (ORNL, USA)
N.Mori, C.Murayama, Y.Ueda (Univ. of Tokyo)
P-156  Diffraction Study on the Nonstoichiometric α-U_{2}N_{3} Phase
H. Serizawa, K. Fukuda, Y. Ishii, S. Funahashi (JAERI)
M. Katsura (Osaka Univ.)

P-157  Cooling Process Dependence of Spin Structure
in the Reentrant Spin Glass Fe_{0.71}Si_{0.29}Al_{2.15}
J. Suzuki (JAERI)
H. R. Child (ORNL, USA)
M. Arai (Kobe Univ.)
Y. Endo (Tohoku Univ.)

P-158  Neutron Scattering Study on Lithium Oxide
Y. Ishii, Y. Morii, S. Funahashi, H. Ohno (JAERI)
R. M. Nicklow (ORNL, USA)

P-159  Refinement of Phonon Eigenvector Phases from Intensities of
Neutron Inelastic Scattering in Si
J. Kulda (ILL, France)
D. Strauch (Univ. of Regensburg, Germany)
Y. Ishii (JAERI)

Session 2: Complex Structure Study with Neutron Probes

P-201  Spinodal Decomposition in Fluid Mixtures
K. Kawasaki, T. Koga (Kyushu Univ.)

P-202  Small Angle Neutron Scattering Study on a Phase Separation
in a 3-Component Microemulsion System
H. Seto, E. Yokoi, S. Komura (Hiroshima Univ.)
D. Schwahn (KFA, Germany)
K. Mortensen (Riso, Denmark)
J. Suzuki, S. Funahashi (JAERI)
Y. Ito (Univ. of Tokyo)

P-203  Neutron Diffraction from Lead Germanate Glasses
N. Umesaki (Government Industrial Res. Inst.)
T. M. Brunier, A. C. Wright (Reading Univ., UK)
A. C. Hamon (RAL, UK)
R. N. Sinclair (Harwell Lab., UK)

P-204  Phase Formation of Physically Associating Polymer Blends
F. Tanaka (Tokyo Univ. of Agriculture and Technology)

P-205  SANS Study of Polymer Chains in Confined Space
H. Hasegawa, H. Tanaka, T. Hashimoto (Kyoto Univ.)
C. C. Han (NIST, USA)
P-206 Microscopic View of the Volume Phase Transition on Weakly Charged Temperature Sensitive Polymer Gels
M. Shibayama (Kyoto Inst. of Tech.)
T. Tanaka (MIT, USA)
C. C. Han (NIST, USA)

578

P-207 Diffractometer for Neutron Crystallography in Biology
Japanese Project
N. Nilmura (Tohoku Univ.)

586

P-208 Structure Study for the Complex of HU Protein and DNA
I. Tanaka, N. Nilmura (Tohoku Univ.)
I. Tanaka (Hokkaido Univ.)
M. Kataoka, K. Mihara, F. Tokunaga (Osaka Univ.)
K. Mika (NIRS)

592

P-209 Small Angle Neutron Scattering Study of the Initial Stage of Lysozyme Crystallization Process
Y. Minesaki, I. Tanaka, N. Nilmura (Tohoku Univ.)
M. Ataka, T. Katsura (Natl. Inst. of Bioscience and Human-technology)

599

P-210 Phase Transitions and Structures of Methylammonium Compounds
O. Yamamura, N. Onoda-Yamamura, T. Matsuo, H. Suga (Osaka Univ.)
T. Kamiyama, H. Asano (Univ. of Tsukuba)
R. M. Illersson, W. I. F. David (RAL, UK)

604

P-211 Structure and Dynamics of Aqueous Electrolyte Solutions by Neutron Scattering
T. Yamaguchi, M. Yamaguchi, H. Wakita (Fukuoka Univ.)
T. Takamuku (TOTO Ltd.)

612

P-212 Ion Dynamics in Molten Meltal Nitrates
T. Kamiyama, Y. Nakamura (Hokkaido Univ.)
K. Shibata, K. Suzuki (Tohoku Univ.)

620

P-213 Double Crystal Diffractometer Arrangement for Very Small Angle Neutron Scattering with PNO in JRR-3M
K. Alzawa, H. Tomimitsu (JAERI)

627

P-214 Phase Separation and Ordering Process in Al-Li Alloys Studied by Small Angle Neutron Scattering and Neutron Diffraction
M. Furusaka (KEK)
S. I. Fujikawa (Tohoku Univ.)
J. M. Tranquada (BNL, USA)

635

P-215 Is there any Correlation between the Intermolecular Structures around Main-group Metal Ion in Liquid and Crystalline States?
K. Ichikawa, Y. Kameda, S. Kotani (Hokkaido Univ.)

641
P-216 Small Angle Neutron Scattering Study of Silica Suspensions
Y. Kimura, M. Kawaguchi (Mie Univ.)
J. Suzuki, S. Funahashi (JAERI)
Y. Isumi (Yamagata Univ.)

P-217 Chain Conformations of ABA Triblock Copolymers in
Microphase-separated Structures for SANS
Y. Matsushita, M. Nomura, J. Watanabe, Y. Mogi, I. Noda (Nagoya Univ.)
C. C. Han (NIST, USA)

P-218 Chain Conformations of the Component Polymers and the Microphase
Separation Structures of Homopolymer/Block Copolymer Blends
N. Torikai, Y. Mogi, Y. Matsushita, I. Noda (Nagoya Univ.)
C. C. Han (NIST, USA)

P-219 Neutron Diffraction Studies of Molten Tl- and Bi-Se Alloys
T. Usuki, Y. Shirakawa, S. Tamaki (Niigata Univ.)
M. Inui, S. Takada (Kyushu Univ.)
K. Sugiyama, Y. Waseda (Tohoku Univ.)

P-220 Neutron Diffraction of Molten Noble Metal Halides
Y. Shirakawa, T. Usuki, S. Tamaki (Niigata Univ.)
M. Inui, S. Takada (Kyushu Univ.)
K. Sugiyama, Y. Waseda (Tohoku Univ.)

P-221 Vesicle Formation in the Block Copolymer/Homopolymer Mixture
Studied by Scattering Methods
S. Koizumi, H. Hasegawa, T. Hashimoto (Kyoto Univ.)
J. Suzuki (JAERI)

P-222 Inversion of the Phase Diagram in Polymer Blends
Studied by Small-angle Neutron Scattering
H. Jinnai, H. Hasegawa, T. Hashimoto (Kyoto Univ.)
C. C. Han (NIST, USA)

P-223 Small-angle Neutron Scattering Study of Amorphous Si-Ti-C-O Fibers
K. Suzuki (KEK)
T. Kamiyama, K. Suzuki (Tohoku Univ.)
Y. Ito (Univ. of Tokyo)
K. Okamura (Univ. of Osaka Pref.)

P-224 Small Angle Neutron Scattering Study of Phase Separation in PMMA/SAN
Y. Ohishi, A. Uemura, M. Minobe (Sumitomo Chem. Co., Ltd.)
K. Puchizaki, J. Suzuki, S. Funahashi (JAERI)

P-225 Low-energy Modes and Medium-Range Correlated Motions
in Pd₃Ge₃-Alloy Glass
K. Shibata, H. Mizuseki, K. Suzuki (Tohoku Univ.)
P-226 Crystallization of Fe_{18}(Cu,Nb)_{30}(Si,B)_{24} Amorphous Alloy
   Studied by Small Angle Neutron Scattering .......................... 709
   M.Ohnuma, Y.Usui, Y.Hamaguchi (Muroran Inst. of Tech.)
   J.Suzuki, S.Funahashi (JAERI)

Session 3: Fundamental Physics Research with Neutron Beam

P-301 Superthermal UCN-production at JAERI – Analysis – ............... 717
   H.M.Shimizu (KEK)
   T.Kawai (KURRI)
   K.Sakai (Tohoku Univ.)

P-302 The Specular Reflection from Multilayer Mirrors to Construct
   the Interferometer for Cold Neutrons ................................ 723
   H.Funahashi (Kyoto Univ.)
   K.Aizawa, H.Tomimatsu (JAERI)
   T.Ebisawa, S.Tasaki (KURRI)
   M.Hashimoto, T.Takahashi (Univ. of Tokyo)
   Y.O.Takahara (Ibaraki Natl. College of Tech.)

P-303 UCN-VCN Facility and Experiments in Kyoto University Reactor .... 729
   Y.Kawabata, K.Okumura, M.Utsuro (KURRI)

P-304 Neutron Optics Using Transverse Field Neutron Spin Echo Method .... 738
   N.Achiwa, M.Hino, Y.Yamauchi, H.Takahara (Kyushu Univ.)
   S.Tasaki, T.Akiyoshi, T.Ebisawa (KURRI)

P-305 Research on Highly Excited States of Nucleus by Slow Neutrons .... 744
   M.Okubo (JAERI)

P-306 PNO-Apparatus and Its Test Use for Neutron Interferometry .......... 752
   H.Tomimatsu, K.Aizawa (JAERI)
   Y.Hasegawa, S.Kikuta (Univ. of Tokyo)

Session 4: Non-scattering Research with Neutron Probes

P-401 JRR-3M Neutron Radiography Facility ................................ 759
   A.Tsuruno, M.Matsubayashi (JAERI)

P-402 Neutron Radiography Research Activities at KURRI .................. 766
   S.Fujino, K.Yoneda, K.Kanda (KURRI)

P-403 Neutron Imaging of Mice and Rats in VIVO with JRR-3 TNRF ........... 775
   G.Matsutomo, K.Ohara (Fujita Health Univ.)
   K.Kato (Inazawa Municipal Hospital)
P-404 Quantitative Neutron Radiography Using Neutron Absorbing Honeycomb
   - Basic Research and Application - ........................................ 780
   M.Tamaki, M.Oda, K.Takahashi, K.Obkubo, K.Tasaka (Nagoya Univ.)
   A.Tsuruno, M.Matsubayashi (JAERI)

P-405 Visualization and Measurement of Fluid Phenomena Using Neutron
   Radiography Techniques ....................................................... 788
   K.Mishima, T.Hibiki, S.Fujine, K.Yoneda, K.Kanda, H.Nishihara (KURRI)
   A.Tsuruno, M.Matsubayashi, M.Sobajima, S.Ohtomo (JAERI)

P-406 Cold Neutron Radiography Using Low Power Accelerator .............. 796
   Y.Kiyanagi, H.Iwasa (Hokkaido Univ.)

P-407 Application of Neutron Radiography to Flow Visualization ............ 802
   N.Takenaka, T.Fujii, A.Ono (Kobe Univ.)
   T.Nakazawa (Kobe Univ. of Mercantile Marine)
   A.Tsuruno (JAERI)

P-408 Classification of Japanese Granitic Rocks and Clays by
   K, Ca, Rb, Sr and its Application to Archaeology .................... 810
   T.Mitsuji (Nara Univ. of Education)

P-409 Reactor Neutron-induced Prompt Gamma-ray Analysis and
   Instrumental Neutron Activation Analysis of Deep Sea
   Sediments in the Pacific and the Japan Sea ................................ 818
   Y.Minai, Y.Ito, T.Tominaga (Univ. of Tokyo)
   C.Yonezawa, M.Hoshi (JAERI)

P-410 Reactor Neutron-induced Prompt Gamma-ray Analysis and
   Instrumental Neutron Activation Analysis of Ancient Glassware .......... 826
   T.Tomizawa (Keio Univ.)
   C.Yonezawa, M.Hoshi (JAERI)
   Y.Minai, Y.Ito, T.Tominaga (Univ. of Tokyo)

P-411 Application of Neutron Radiography to Plant Research
   and Water Hydrology in Soil ............................................. 834
   T.M.Nakanishi, S.Matsumoto, H.Matsumoto, A.Yasunishi (Univ. of Tokyo)
   H.Kobayashi (Rikkyo Univ.)
   A.Tsuruno (JAERI)

P-412 The Cadmium Content in Bone of Osteoporotic Patients ............... 841
   M.Terai, K.Iizuka (Otsuka Women's Univ.)
   M.Eguchi (Kanto Rosai Hospital)

P-413 High Quality Neutron Radiography Imaging Using Cooled CCD Camera
   - Tomography - ......................................................... 846
   H.Kobayashi (Rikkyo Univ.)
Session 5: Novel Application of Neutron Beam

P-501 Utilization of Thymine Analogue as a Boron Carrier for Neutron Capture Therapy
Z.H.Zhang, Y.Oda, M.Takagaki, H.Kikuchi (Kyoto Univ.)
T.Kobayashi, K.Kanda, K.Ono (KURRI)

P-502 Electron-ion Correlation in Liquid Te II
S.Takeda, M.Inui (Kyushu Univ.)
S.Tamaki, K.Maruyama (Nihgata Univ.)
Y.Waseda (Tohoku Univ.)

P-503 Gadolinium Neutron Capture Therapy: Preclinical Studies
Y.Akine, N.Tokita, K.Tokunye, M.Sato, H.Churei
(The Natl. Cancer Center Hospital)

P-504 Growth Inhibition of Human Pancreatic Cancer Grafts in Nude Mice by Boron Neutron Capture Therapy
H.Yanagie, Y.Fujii, K.Kosaki, Y.Saegusa, T.Tomita, M.Sekiguchi (Univ. of Tokyo)
H.Kobayashi (Rikkyo Univ.)

P-505 Phantom Experiment of Depth-dose Distributions for Gadolinium Neutron Capture Therapy
T.Matsumoto, K.Kato, Y.Sakuma (Musashi Inst. of Tech.)
A.Tsuruno, M.Matsubayashi (JAERI)

P-506 Prompt Gamma-ray Spectrometry for Measurement of B-10 Concentration in Brain Tissue and Blood - Clinical Use and Experimental Study -
Y.Nakagawa, K.Kitamura (Natl. Kagawa Children's Hospital)
T.Kobayashi (KURRI)
K.Matsumoto (Tokushima Univ.)
H.Hatanaka (Teikyo Univ.)

P-507 Boron Neutron Capture Therapy for Children with Malignant Brain Tumor
Y.Nakagawa, H.Komatsu, T.Kageji (Natl. Kagawa Children's Hospital)
F.Tsuij (Natl. Okayama Hospital)
K.Matsumoto, K.Kitamura (Tokushima Univ.)
H.Hatanaka, T.Minobe (Teikyo Univ.)

P-508 Structure Analysis of K,H(SO₄) by Neutron Powder Diffraction
S.Murakami, Y.Kuroiwa, Y.Noda (Chiba Univ.)
Y.Nakai, T.Kamiyama, H.Asano (Univ. of Tsukuba)
P-509 Study of Neutron Medical Irradiation Facility with
Supermirror Neutron Guide Tube in JRR-3M
K.Soyama, M.Suzuki, H.Ichikawa (JAERI)
Y.Kawabata (KURRI)

P-510 Progress in Study of a Medical Reactor
for Boron Neutron Capture Therapy
M.Sasaki, J.Hirota (MAPI)
S.Tamao (MHI)
K.Kanda (KURRI)
Y.Mishima (MISHIMA Inst. for Dermatological Res.)

P-511 Neutron Diffraction Topographic Observation of
Ni-base Superalloy Single Crystals
H.Tominaga, K.Aizawa (JAERI)
K.Iijima, A.Yoshinari (Hitachi Ltd.)

P-512 Diffraction Plane Dependency of Elastic Constants in Ferritic Steel
in Neutron Stress Measurement
M.Hayashi, M.Ishiwata (Hitachi Ltd.)
N.Minakawa, S.Funahashi (JAERI)

P-513 X-ray Residual Stress Measurement and Its Variation during Plane
Bending Fatigue and Sliding Wear Processes in TiC,TiN,TiB2 and
Al2O3 Coated Carbon Steels
T.Endoh, K.Idemitsu, M.Kawakami (Tokai Univ.)

Session 6: Technical Innovation of Neutron Beam Experiment

P-601 Application of Neutron Spin Echo Spectroscopy to Dynamical Behaviors
of Condensed Matter
S.Komura, T.Takeda, H.Seto (Hiroshima Univ.)

P-602 Neutron Spin Echo Spectrometer at JRR-3M
T.Takeda, S.Komura, H.Seto, M.Nagai, H.Kobayashi, E.Yokoi (Hiroshima Univ.)
T.Ebisawa, S.Tasaki (KURRI)

P-603 Practical Conditions in the Neutron Diffraction under High Pressure
K.Kamigaki, M.Ohashi (Tohoku Univ.)

P-604 Neutron Scattering Cross Sections of Liquid Hydrogen and Deuterium
for Cold Neutron Production
N.Morishima, D.Mizobuchi (Kyoto Univ.)

P-605 High Pressure Apparatus for Neutron Diffraction Study
G.Oomi (Kumamoto Univ.)
Y.Shiozaki (Hokkaido Univ.)
<table>
<thead>
<tr>
<th>Paper</th>
<th>Title</th>
<th>Authors</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-606</td>
<td>Polarized Thermal Neutron Field around Polarized Helium-3 Gas Cells in a Nuclear Reactor</td>
<td>K. Ishikawa, T. Iguchi, M. Nakazawa (Univ. of Tokyo)</td>
<td>989</td>
</tr>
<tr>
<td>P-607</td>
<td>Thermo-lumino Detector for a Neutron Diffraction</td>
<td>M. Hidaka, T. Morisako (Kyushu Univ.) M. Nishi (Univ. of Tokyo)</td>
<td>997</td>
</tr>
<tr>
<td>P-609</td>
<td>Neutron Measurements as Fusion Plasma Diagnostics</td>
<td>T. Nishitani (JAERI) M. Hoek (JAERI, STA Fellow)</td>
<td>1009</td>
</tr>
<tr>
<td>P-610</td>
<td>Current Status and Future Utilization in Research Reactors</td>
<td>Y. Koyama, Y. Hoshi, D. Nemoto, H. Takahashi (JAERI)</td>
<td>1017</td>
</tr>
<tr>
<td></td>
<td>Authors Index</td>
<td></td>
<td>1027</td>
</tr>
</tbody>
</table>
NEUTRON DIFFRACTION STUDY IN AgCrO$_2$

"Yasuaki OOHARA, Hideki YOSHIZAWA, Setsuo MITSUDA, Nariyasu YAGUCHI, Hideaki KURIYAMA, Takayuki ASANO and Mamoru MEKATA

*Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo, 106 Japan

†Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162 Japan

‡Faculty of Engineering, Fukui University, Bunkyo, Fukui, 910 Japan

ABSTRACT

The magnetic ordering of AgCrO$_2$, a rhombohedrally stacked triangular lattice antiferromagnet with Heisenberg spin $S=3/2$, has been studied by neutron diffraction on powder samples. The magnetic phase transition temperature is determined to be 24 K. The magnetic peaks appear at (0.327, 0.327, 0) in the hexagonal units, showing that the magnetic structure is a modulated 120° structure. The modulation is due to the competitions between the in-plane and out-of-plane interactions. The magnetic peaks are broad, indicating that these strong competitions suppress the development of the true long-range order in AgCrO$_2$ below 24K.

INTRODUCTIONS

Magnetic properties of ABO$_2$ compounds with the delafossite structure have taken much attention for these years. These compounds are rhombohedrally stacked triangular lattice antiferromagnets, of which the spin Hamiltonian can be written as
\[ H = -2J_1 \sum_{<i,j>} S_i \cdot S_j - 2J'_1 \sum_{<i,j>} S_i \cdot S_j + D \sum_i (S_i^2)^2 \]  

where \( J_1 \) (<0) and \( J'_1 \) are the nearest neighbour in-plane and out-of-plane interactions, respectively, and \( D \) is an anisotropy constant. (Fig.1) Because the exchange path of the out-of-plane interaction \( J'_1 \), B-O-A-O-B, is much longer than that of the in-plane interaction \( J_1 \), B-B and B-O-B, the magnitude of \( J_1 \) is much larger than that of \( J'_1 \). Thus, an ABO\(_2\) compound has been studied as a realization of a two-dimensional triangular antiferromagnet. In a Heisenberg two-dimensional triangular antiferromagnet, a short-range order of a 120° structure develops as temperature decreases, but no long-range order exists at a finite temperature. The weak out-of-plane interaction \( J'_1 \), however, develops the coherence among layers and then the ABO\(_2\) compound exhibits three-dimensional ordering. In this sense, as long as the magnetic ordering and the phase transition are concerned, the ABO\(_2\) compound should be regard as a rhombohedral antiferromagnet, rather than a two-dimensional triangular antiferromagnet. Rastelli and Tassi showed theoretically that the degenerate helical ordering, where the modulation vector \( Q \) takes a continuous value, occurs in a Heisenberg rhombohedral antiferromagnet.\(^{79}\) For a vanishing but none-zero \( J'_1/J_1 \), \( Q \) runs along the line of \((1/3 1/3 z)\) in the hexagonal units. Assuming that the distribution of \( Q \) is uniform along the \((1/3 1/3 z)\) line for all the helical ordering, corresponding to a 120° spin structure in the \( c \)-plane, magnetic peaks appear at \((h/3 h/3 0)\), where \( h \) is integer, with a tail extending in the direction of increasing 2\( \theta \). It should be noted that these patterns of Bragg
peaks do not result from the uncorrelated stacking of ordered planes as is observed in a two-dimensional magnet, but result from the degenerate helices.

In Rastelli and Tassi's discussion, only $J_1$ and $J_1'$ are taken into account. For a family of $ABO_3$ compounds, however, there are other interactions which can be larger than $J_1'$. From the inspection of the exchange path, we expect that the in-plane second- and third-nearest neighbour interactions, $J_2$ and $J_3$, must be larger than $J_1'$. When these interactions are taken into account in the Hamiltonian, eq. (1), the infinite degeneracy will be removed, although Rastelli and Tassi claimed that quantum effects may restore the infinite degeneracy.\(^5\)

Recently, Kadowaki et al. measured the neutron diffraction pattern of a powder sample of CuCrO$_2$, an $S=3/2$ Heisenberg rhombohedral antiferromagnet.\(^3\) They observed magnetic peaks indexed by $(1/3 \ 1/3 \ l)$ and $(2/3 \ 2/3 \ l)$ ($l$: integer). It shows that the infinite degeneracy is removed because peaks indexed by only $(1/3 \ 1/3 \ 0)$ and $(2/3 \ 2/3 \ 0)$ are allowed when the infinite degeneracy exists. From the integrated intensities of these peaks, the magnetic structure is determined to be such that a unit cell consists of three layers of the $ac$-$120^\circ$ spin structure, indicating a small Ising anisotropy of CuCrO$_2$, although the phase relation between three layers remains undetermined.

In this paper, we report the neutron scattering measurements on powder samples of AgCrO$_2$. AgCrO$_2$ is an isostructural and iso spin system with CuCrO$_2$, and its $J_1$ and $T_N$ are reported to be $J_1=11.4$K and $T_N=30$K,\(^3\) which are very close to those of CuCrO$_2$. Nevertheless, as is shown below, its magnetic peaks cannot be indexed by $(h/3 \ h/3 \ l)$.

**EXPERIMENTAL PROCEDURE**

The powder samples of AgCrO$_2$ were prepared by two methods: flux reaction $(\text{AgNO}_3+\text{LiCrO}_2\rightarrow\text{AgCrO}_2+\text{LiNO}_3)$,\(^11\) and oxidization in an oxygen atmosphere $(2\text{Ag}+\text{Cr}_2\text{O}_3+1/2\text{O}_2\rightarrow2\text{AgCrO}_2)$.\(^12\) No appreciable difference in results has been found between samples prepared by the two methods.

The neutron scattering experiments were performed with the ISSP triple-axis spectrometer 4G installed at JRR-3M JAERI (Tokai) with the double-axis mode. Although incident neutrons with several wave numbers and collimations were used, we obtained the typical data as follows. An incident neutron with a wave number $k_i = 4.27$ Å$^{-1}$ was obtained by the pyrolytic graphite $(002)$ reflection. Higher-order neutrons were removed by a pyrolytic graphite filter. The collimation of $40^\circ$-$20^\circ$-$20^\circ$ was employed. 10 cc of the sample was mounted in a closed cycle He-refrigerator.

**RESULTS and DISCUSSION**
Powder diffraction patterns were measured at several temperatures. Figure 2 shows the results at 8K, 30K and 300K. At 8K, three magnetic peaks appear. The temperature dependence of the peak intensities at $M_1$, $M_2$ and $M_3$ is shown in Fig. 3. In the figure, one can see an anomaly corresponding to the magnetic phase transition at 24K±1. A broad bump in the 26 scan observed at 30K, above $T_N$, indicates a well-developed short-range magnetic-order in two-dimensional triangular lattice planes, which remains above 80K as the long tail of the temperature dependence.

These peaks, $M_1$, $M_2$ and $M_3$ show a small but distinct deviation from the (1/3 1/3 l) positions, (l:integer) indicating that the infinite degeneracy is lifted and the 120° structure is modulated. If the second-nearest neighbour interaction in the $c$-plane is taken into account, the modulation vector either $(Q Q 0)$ or $(Q Q 3/2)$ can be seen. Further in-plane interactions do not change the situation as long as only $J'_1$ is taken into account as the out-of-plane interaction. Therefore, we attempted to assign $M_1$, $M_2$ and $M_3$ to $(Q Q 0)$ and equivalent positions in the reciprocal space, namely to $(Q+h Q+k -2h-k+3l)$, where $h$, $k$ and $l$ are integers, and also to $(Q Q 3/2)$ and equivalent positions. In the former, the resultant parameter is $Q = 0.327$, which excellently accounts for the observed peaks $M_1$, $M_2$ and $M_3$ by $(Q Q 0)$, $(Q Q-1 1)$ and $(Q-Q 1 0)$.
(Q-1 Q 2) as shown in fig. 4. In the latter choice of l, the fitting is failed for any Q.

Widths of the magnetic peaks are apparently wider than those of nuclear peaks at (0 0 3) and (0 0 6), solely determined by the instrumental resolution. This broadening is due to neither the infinite degeneracy nor two-dimensionality of this compound because in these cases an asymmetric line shape which extends only to the direction of higher 2θ is expected. In the present data, however, the broadening is symmetric and extends to both side of the peaks. It suggests that even in the c-plane the development of the long-range order in AgCrO₂ is suppressed. For the ABO₃ compound which shows the 120° spin structure such as CuCrO₂, the spin correlation in the c-plane is well developed.⁴ We believe that the strong spin-fluctuations in the c-plane seem to be associated with the modulation of the 120° structure as explained below.

Now we explain why the distribution of the modulation vector Q exists when the 120° structure is modulated. The energy with the modulation vector (Q Q 0) for Q<1/3 is written as

\[
E = NS^2 \left\{ -16J_3 u^4 - 16(J_2 - 2J_3)u^3 - 4(4J_3 - 6J_2 + J_1)u^2 \\
- 4J_1' u + 3J_1 - 6J_2 + 3J_3 \right\}, \tag{2}
\]

where N is the number of the magnetic ions, \( u = \cos(2\pi Q) + 1/2 \) and \( J_1' \) is positive. The exchange path of \( J_5, \text{Cr-O-Cr} \), is similar to that of \( J_2 \), and we expect the magnitude of the exchange interaction is the same order. By the condition that E takes the minimum at \( u_0 \) corresponding to the observed modulation vector, i.e.,

\[
\frac{\partial E}{\partial u} \bigg|_{u = u_0} = 0,
\]

the relation between \( J_1, J_2, J_3, J_1' \)

and \( u_0 \) is obtained as

\[
J_1' = -2(4J_3 - 6J_2 + J_1)u_0 - 12(J_2 - 2J_3)u_0^2 - 16J_3u_0^3. \tag{3}
\]

When the 120° structure is modulated, \( u_0 \) has none zero value. (In the case of \( Q=0.327, u_0=0.035 \).) Because \( J_1' < < J_1, J_2 \) and \( J_3 \), the coefficient of the first term must be almost zero, and that of the second one must be small. Then, when E is expanded as

\[
E = a_0 + \sum_{n=2}^{4} a_n (u - u_0)^n. \tag{4}
\]
one finds that eq.(3) yields a strong constraint that
\[ a_2 = \frac{1}{2} \frac{\partial^2 E}{\partial u^2}, \]
is very small. Simultaneously, \( a_3 \) must be the same order of \( a_2 \) at most, required from \( E \) taking the minimum value at \( u_0 \). Consequently, the eq.(4) allows the existence of many other \( Q \)'s whose energies are very close to that of \( Q = 0.327 \). Clearly, thermal fluctuations excite a number of different \( Q \)'s, resulting in the distribution of the modulation vector \( Q \).

In conclusion, we have carried out the neutron diffraction on AgCrO\(_2\). The magnetic phase transition temperature \( T_N \) is determined to be 24K. The magnetic structure is a modulated 120° structure, characterized by the modulation vector \((0.327, 0.327, 0)\). It can be explained by the competitions among the in-plane and out-of-plane interactions. These strong competitions suppress the development of the true long-range order in AgCrO\(_2\) below \( T_N \).

We would like to thank Dr. H. Kadowaki for valuable discussions.

References

CRYSTAL FIELD SPLITTING IN CeAs AND CeP UNDER HIGH PRESSURE

°Yasuaki OOHARA, °Yasushi OKAYAMA, °Hiroki TAKAHASHI,
°Hideki YOSHIZAWA, °Nobuo MÔRI, *Setsuo MITSUDA,
†Toyotaka OSKABE, †Yoshinori HAGA, †Masahumi KOHGI and
†Takashi SUZUKI

°Institute for Solid State Physics,
University of Tokyo
Roppongi, Tokyo, 106 Japan

*Faculty of Science,
Science University of Tokyo
Kagurazaka, Shinjuku-ku, Tokyo, 162 Japan

†Faculty of Science
Tohoku University
Aoba-ku, Sendai, 980 Japan

ABSTRACT

The crystal field splitting in CeAs and CeP under high pressure has been measured by inelastic scattering. In CeAs, the crystal field splitting, $\Delta^g$, between the quartet $\Gamma^g$ and the doublet $\Gamma^s$, is almost constant ($\approx 13$ meV) up to 2.0 GPa, suggesting the doublet $\Gamma^s$ remains in the ground state. However, $\Delta^g$ decreases drastically at 2.5 GPa, where the antiferromagnetic moment decreases extremely. The same tendency is observed in CeP.

INTRODUCTIONS

CeAs is NaCl-type crystal and known as a very low carrier heavy fermion material. It exhibits a type-I antiferromagnet ordering (AF-I) below 8K, where ferromagnetic (001) planes are stacked in a $+--+$ sequence. However, applying the hydrostatic pressure, the new magnetic ordering (AF-I') in which a ferromagnetic component is superimposed on an AF-I structure appears above the critical pressure, $P_c=1.1$ GPa. Although a definite magnetic structure for $P>P_c$ has not been determined yet, one of the
possible magnetic structure is "+ 0 + 0" structure, where the ferromagnetic
(001) plane and the paramagnetic (001) plane are stacked by turns. (fig. 2) A
similar kind of the magnetic structure which consists of ferromagnetic (001)
planes and paramagnetic (001) planes, "+ 0 - " (fig. 3) etc., is seen in the
magnetic ordering of CeSb,3 isomorphous to CeAs.

Fig.1 AF-1 structure. Fig. 2 "+ 0 + 0" structure. Fig. 3 "+ 0 - " structure.

In CeX, the octahedral
crystal field splits the \( ^2F_{5/2} \)
multiplet of the 4f electron into a
doublet \( \Gamma_7 \) and a quartet \( \Gamma_8 \) (fig.4)

In the paramagnetic state, the
ground state of CeSb is the doublet \( \Gamma_7 \). However, according to Rosse-
Mignot et al, the ground state of the ferromagnetic plane is the quartet \( \Gamma_8 \),
although the ground state of the paramagnetic plane in the ordered state is still
the doublet \( \Gamma_7 \).3,4 Such an inversion of the ground state in CeSb is explained
by the p-f mixing mechanism.5

In this paper, we report the crystal field splitting in CeAs under high
pressure to see if the inversion of the ground state occurs in the AF-I'
structure as in CeSb. We also report the measurement of the crystal field
splitting in CeP under high pressure, which exhibits the AF-I' structure above
Pc (=0.25 GPa) as well.6

**EXPERIMENTAL PROCEDURE**

The neutron scattering experiments were performed with the ISSP
triple-axis spectrometer 4G installed at JRR-3M JAERI (Tokai). The neutron
energy-loss configuration was chosen. An incident neutron energy was fixed at
30 meV or 34.2 meV, using by the pyrolytic graphite (0 0 2) reflection.
Higher-order neutrons were removed by the pyrolytic graphite filter.
Collimations of 40'-80'-40'-80', 40'-open-40'-40', 40'-40'-40'-40' were employed. The pyrolytic graphite (0 0 2) reflection was also used for analyzing neutron energy. The length of the scattering vector was fixed to \( l (1 1 0) l \). The 0.5 cc powder samples of CeAs and CeP were sealed in a aluminium cell with fluorinate and placed in Macwan cell. A \(^4\)He cryostat was used for cooling the samples.

**EXPERIMENTAL RESULTS**

Measurements were done at 8 K and some higher temperatures, 40 K and 80 K, at every pressure. As the temperature was increased, no significant changes were observed except broadening of the line width. Typical data obtained at 8K are shown below.

Figure 5 shows spectra of CeAs (a) at ambient pressure and (b) 2.5 GPa. The peak position, corresponding to the crystal field splitting \( \Delta_7^8 \), is well observed. The obtained \( \Delta_7^8 \), at ambient pressure is 13 meV, which is in good agreement with the reported value.\(^7\) The peak position at 2.5 GPa is lower than that at ambient pressure, but line width at 2.5 GPa is clearly broader. Figure 6 (a) shows the pressure dependence of the crystal field splitting \( \Delta_7^8 \) and line widths \( \Gamma \), obtained from the Lorentzian fitting. The crystal field splitting is almost independent of pressure until 2.0 GPa. Above 2.0 GPa, \( \Delta_7^8 \) decreases progressively as the applied pressure increases. The line width seems to increase monotonically from ambient pressure.

![Graphs showing spectra of CeAs](image)

**Fig. 5** Spectra of CeAs at (a) ambient pressure and (b) 2.5GPa.

Figure 6 (b) shows the pressure dependence of the crystal field splitting and the line width of CeP. The obtained \( \Delta_7^8 \) at ambient pressure is 14 meV in good agreement with the reported result.\(^7\) As was observed for CeAs, there is no drastic change at Pc for CeP as seen from the figure. \( \Delta_7^8 \) falls down from 14 meV to 10 meV at around 1 G. However, \( \Delta_7^8 \) is almost the same value from 2.0 Gpa to 2.5 GPa. The line width becomes maximum at around 1 GPa.
Fig. 6 Pressure dependence of the crystal field splitting and line width (FWHM) of (a) CeAs and (b) CeP.

DISCUSSION

The ground states of CeAs and CeP are the doublet $\Gamma$, at ambient pressure.\(^{1,7}\) Judging from the experimental result, $\Delta^8$ of CeAs as well as CeP is considerably large compared with that of CeSb in the paramagnetic state ($\sim$4 meV)\(^{13,4,7}\) and no drastic softening was observed. Thus, we exclude the possibility of the inversion of the ground state at Pc for both CeAs and CeP.

Now we consider the rapid decreasing of $\Delta^8$ at 2.5 GPa of CeAs. Theoretical study shows that the crystal field splitting $\Delta^8$ is derived not only from Coulomb interactions by the point charge model, but also from the various mixing effects.\(^{5,8}\) Since there is no great change of the lattice parameters at 2.5 GPa, the Coulomb interactions cannot be responsible for the decreasing of $\Delta^8$. Thus, the strong mixing effect which reduces $\Delta^8$ will exist at 2.5 GPa. It also influence the magnetic structure. The antiferromagnetic moment decreases extremely at 2.5 GPa.\(^{9}\)

In CeP, the rapid decreasing of $\Delta^8$ at around 1 GPa seems to be also due to growing the mixing effect. The line width shows the maximum at around 1 GPa, although the degree of the softening is weaker than that of CeAs. What causes the broadening is an open question at the moment.

More detailed study including the elastic scattering at high pressure is under way.
REFERENCES

9) Y. Oohara et al.: unpublished.
LATTICE INSTABILITY OF HIGH-Tc OXIDE SUPERCONDUCTORS STUDIED BY INELASTIC NEUTRON SCATTERING


1 Department of Physics, Kobe University, Rokkodai, Nada, Kobe 657, Japan
2 Department of Physics, Tohoku University, Aramaki, Aoba, Sendai 980, Japan
3 Institute of Material Research, Tohoku University, Katahira, Sendai 980, Japan
4 Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK
5 NTT Applied Electronics Laboratories, Tokai, Ibaraki, Japan

Measurements of S(Q,E) over a wide range of Q-E space were performed on superconducting La1.85Sr0.15CuO4 and YBa2Cu3O7 using a high energy-resolution neutron chopper spectrometer MARI installed at the Rutherford Appleton Laboratory in UK. Fine structures in their phonon density of states as well as the Q-dependences of excitation were well revealed. The Q-dependence of S(Q,E) is very susceptible to a local structural change on going into superconducting state and showed an anomalous behaviour at T=Tc similar to a critical phenomena. In order to understand the physical meaning of the observation, we have developed a new data analysis scheme to obtain Dynamical Pair Correlation Function (DPCF) by taking Fourier transformation of S(Q,E) in some energy band. From the DPCF we found below Tc a <110> buckling motion of the pyramid structure and the shortening of the distance between the apical oxygen and the copper atom in the plane.

§ 1. Introduction
Recent development of pulsed neutron scattering technique has enabled us to observe S(Q,E) in a very wide range of Q-E space [1]. We found that S(Q,E) is very sensitive to the local structural evolution as we reported in [2]. S(Q,E) of a powder sample at the typical energy showed anomalous behavior at Tc. A drastic change occurs in the Q-dependence of S(Q,E) of YBa2Cu3O7 for the apical oxygen mode parallel to the c-axis. In [2] we suggested from a model calculation that a <110> buckling local structure or motion of the O(4)-Cu(2)-O(2)-O(3) pyramid is created with a critical behaviour at Tc, expansion of the correlation length. Therefore we have extended the study to observe the existence of the similar behavior for different system, La1.85Sr0.15CuO4, in order to prove the common mechanism for high-Tc superconductivity. We have also developed a model-independent analysis scheme for S(Q,E) to get dynamic pair correlation function (DPCF) between specific atoms. In this paper we demonstrate how we can extract a local structural instability and show the strong relation between it and the superconductivity.

§ 2. Experiment
Neutron inelastic scattering measurements were carried out on the chopper spectrometer MARI [1] installed at the ISIS facility of Rutherford Appleton Laboratory under UK-Japan collaboration on neutron scattering research. The spectrometer covers the wide scattering angle from 3° to 135° with 550 detectors. The employable incident energy is from 20meV to 1eV with the energy resolution of 1.2% of the incident energy. The measurement was done by Time-of-Flight method. Thus the spectrometer gives two dimensional and continuous S(Q,E) in a very wide range of Q-E space with huge amount of data points, 8 Mega-bytes for one data-set. We used a disk shape sample, 8cm in diameter and 8mm in thickness, for YBa2Cu3O7 and hollow annular sample, 4cm in outer-diam and 3cm in inner-diam. These amount of samples gives considerable multiple-scattering, thus we used to estimate it by the multiple-scattering Monte Carlo simulation program MSCAT [3]. More importantly we corrected scattering from multi-
phonon effect by the exact calculation for two-phonon process and took the approximation for higher-phonon scattering [4]. We employed two different incident energies of 130meV and 200meV for both samples.

In Fig.1 we show the entire $S(Q,E)$ of $La_{1.85}Sr_{0.15}CuO_4$ for $E_i=200\text{meV}$ at 50K. It is clearly seen the optical mode, which has the shape of a mountain ridge in a map. In Fig. 2 (a) the $Q$-dependence of $S(Q,E)$ of $La_{1.85}Sr_{0.15}CuO_4$ integrated between 50 and 90meV and in Fig. 2(b) that of $YBa_2Cu_3O_7$ integrated between 40 and 90meV. There is prominent change in the $Q$-dependence at $T_c$; the amplitude of the oscillation is enhanced. This corresponds to the expansion of the correlation length at $T_c$ as we discussed in [2]. Furthermore the details of the $Q$-variation changes. In [2] we explained this by applying a model calculation. It may be, however, dependent to the intended starting model structure. Therefore we have developed a new data analysis scheme to characterize the structural evolution appeared in $S(Q,E)$ as we will discuss in the next section.

Fig. 2 (a) $Q$-dependence of $S(Q,E)$ of $La_{1.85}Sr_{0.15}CuO_4$ integrated from 50 to 90meV comparing the data below, above and $T=T_c$. (b) $Q$-dependence of $S(Q,E)$ of $YBa_2Cu_3O_7$ integrated from 57.5 to 65meV.
§ 3. Dynamic Pair Correlation Function

The continuous two dimensional $S(Q,E)$ data has given a unique opportunity to explore the huge information on dynamic aspect of material. And hence we have developed a new data analysis scheme to obtain a dynamic correlation function from $S(Q,E)$ [5]. Here we briefly summarize the method for a mono-atomic system. For single phonon scattering, $S(Q,E)$ is written in the form

\[ S(Q,E) = A \left[ 1 + \frac{1}{N} \sum_{i \neq i'} <\eta_i \cdot \eta_{i'}> e^{iQ(i - i')} \right] <Q> \]  \hspace{1cm} (1)

where $A$ is $\frac{r^2 Q^2}{2M} e^{2W \frac{\eta(E) + 1}{E}}$ and $\eta_i$ is the directional cosine of the displacement vector of the $i$th atom to the scattering vector $Q$. The $<Q>$ stands for taking an average for the $Q$-direction. By taking the Fourier transform of the distinct term, i.e. second term, analogous to the conventional diffraction data analysis for glassy systems, we get the Dynamic Pair Correlation Function (DPCF or $Dd(r,E)$) at an excitation energy $E$:

\[ Dd(r,E) = \frac{2}{\pi} \int_{0}^{\infty} Q \left( S(Q,E)/A \cdot 1 \right) \sin (rQ) dQ \] \hspace{1cm} (2)

The DPCF contains information on the atomic pair correlation weighted by a factor proportional to the neutron scattering length and additionally weighted at the relevant energy by $<\eta_i \cdot \eta_{i'}>$. The important assumption to obtain a meaningful DPCF by this procedure is that the relevant phonon dispersion is sufficiently flat, so that it does not go out of the energy band used to integrate $S(Q,E)$ prior to the Fourier transformation. We should note that the O-O correlations are most enhanced in the DPCF because of the smaller mass of oxygen; in comparison for the diffraction data Cu-Cu, Cu-Y and La-Cu correlations are most enhanced. Therefore we expect the DPCF to be very sensitive to some local structural change relevant to the oxygens, whereas the diffraction data is insensitive to such a change since it is dominated by contributions from other atom pairs.

![Graph](image)

Fig. 3 Dynamic pair correlation function $Dd(r, E)$ of YBa$_2$Cu$_3$O$_7$ at 83, 93 and 113K. Prominent changes are marked by arrows $a$, $b$ and $c$. 

— 210 —
In Fig. 3 the DPCF of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) integrated from 40meV to 90meV is depicted for the temperature above, below and at \( T_c = 93K \). The Q-range used for the Fourier transform is 2.5 to 12\( \AA^{-1} \). The statistical error is drawn only for the data at \( T = T_c = 93K \). We examined the effect of the truncation error on the Fourier transform by changing the Q-range as well as the effect of the fitting in estimating the pre-factor \( A \) in eq. (1) by changing \( A \) artificially. We found that these manipulations have an effect on the amplitude of the oscillation only for \( r \) smaller than 1–2 \( \AA \) and therefore the evolution, e.g. peak split and peak shift, in the DPCF at different temperatures, say above 2\( \AA \), is an intrinsic feature due to the structural distortion. We can find the prominent peaks in \( Dd(r,E) \) at 2.7, 4.1, 5.4, 6.5 and 8.0 \( \AA \) in Fig. 3, which correspond to the typical distance between oxygens, cf. Fig.4.

In Fig. 3 we can recognize three substantial evolution in the DPCF across \( T_c \) and these are summarized in Fig.4.

1. The peak around 2.7\( \AA \) separates below \( T_c \) into two peaks at 2.5\( \AA \) and 3.1\( \AA \). (marked \( a \)). This evolution may correspond to the \( <110> \) buckling of the \( \text{Cu}(2)-\text{O}(2)-\text{O}(3) \) plane with a movement of 0.15\( \AA \) for individual oxygen atoms alternately in opposite directions out of the plane. The buckling creates two different distances in the \( c \)-direction between \( \text{O}(2) \) and \( \text{O}(2) \) or between \( \text{O}(3) \) and \( \text{O}(3) \).

2. A shoulder appears at 3.6\( \AA \) only at \( T_c \). (marked \( b \)). Possibly the \( \text{O}(4) \) atom fluctuates and moves toward the \( <110> \) direction. The distance, normally 3.9\( \AA \), between \( \text{O}(4) \) and the nearest \( \text{O}(4) \) along the \( a \)-axis or the \( b \)-axis is shortened by 0.3\( \AA \) by this movement. Thus the movement of \( \text{O}(4) \) in the \( <110> \) direction is about 0.5\( \AA \), which is about 14% of the \( a \) or the \( b \) lattice constants, and this is consistent with the preliminary estimate in [2]. We could, however, explain also the evolution at 3.6\( \AA \) in terms of an anomalous "zigzag" mode of \( \text{O}(1) \) on the chain site [6].

3. The peak at 8.1\( \AA \) above \( T_c \), which corresponds to correlation along the \( c \)-axis between the two \( \text{O}(4) \) above and below the yttrium layer, becomes a double peak at \( T_c \) and shifts to 7.9\( \AA \) below \( T_c \). (marked \( c \)). Hence, the \( \text{O}(4) \) atom has a strong fluctuation at \( T_c \) along the \( c \)-axis also. Below \( T_c \), \( \text{O}(4) \) moves close toward \( \text{Cu}(2) \) by 0.1\( \AA \) (though we should note that our observation is of a shortening of the \( \text{O}(4)-\text{O}(4) \) distance and not a direct measurement of the \( \text{Cu}(2)-\text{O}(4) \) distance). Mustre de Leon et al. [7] reported that there are two possible sites for \( \text{O}(4) \) separated by 0.13\( \AA \). Our observations confirm their results.

§ 4. Discussion

By combining to our recent results [8] we found that the structural instability observed here likely correspond to a soft phonon mode or an anharmonic rotational motion in a double-well potential of the rigid unit of a pyramid structure for \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). This type of structural instability in a double-well potential is well known from the dynamical phase transition of perovskite type structures [9,10]. More importantly below \( T_c \) the apical \( \text{O}(4) \) shifts down close to the \( \text{Cu}(2) \) plane by 0.1\( \AA \). The distance between \( \text{Cu}(2) \) and \( \text{O}(4) \) is very closely connected to the superconductivity [7,11], and the shortening may drastically induce hole-charge transfer to the Cu-O plane.

The structural instability we observed here is dynamic, confined in a local or short-range region and incoherent, so it is very difficult to observe by a conventional diffraction technique. In this paper we have demonstrated that the DPCF is very sensitive to such physical phenomena, and we have been able to explain the entire picture of the structural instability of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). The study of the DPCF of \( \text{La}_{1.85}\text{Sr}_{0.15}\text{Cu}_2\text{O}_4 \) is under way. We speculate that the very similar structural instability is taken place in this material too according to the similarity of the temperature evolution in the Q-dependence of \( S(Q,E) \) as that of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \).
Fig. 4 Schematic crystal structure of YBa$_2$Cu$_3$O$_7$. Typical distances between atoms are specified in angstrom. Motion of the atoms in a pair of pyramids is specified by the solid arrows.

REFERENCES
STRUCTURAL PHASE TRANSITIONS OF NaV₆O₁₁ AND SrV₆O₁₁

°Yasushi KANKE, °Fujio IZUMI, °Yukio MORII, °Satoru FUNAHASHI, #Etso AKIBA and °Katsuo KATO

°National Institute for Research in Inorganic Materials
1-1 Namiki, Tsukuba, Ibaraki 305, Japan

*Department of Physics, Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki 319-11, Japan

#National Chemical Laboratory for Industry
1-1 Higashi, Tsukuba, Ibaraki 305, Japan

ABSTRACT

Crystal structures of NaV₆O₁₁ and SrV₆O₁₁ at several temperatures were studied by either Rietveld analyses of both neutron and X-ray powder diffraction data, or an analysis of X-ray single crystal diffraction data. At 200 K, NaV₆O₁₁ loses the center of symmetry, and its space group changes from P6₃/mmc to P6₃mc. Consequently, V(2) splits into two sites. At 30 K, NaV₆O₁₁ was transformed from the hexagonal form to the orthorhombic one (Cmc2₁), and V(1) splits into two sites. These results indicate that magnetic phase transitions of NaV₆O₁₁ at 245 K and 64.2 K are accompanied by structural phase transitions. On the other hand, no structural phase transition was detected in SrV₆O₁₁.

INTRODUCTION

NaV₆O₁₁ was firstly synthesized by De Roy et al.¹ and revealed to be structurally related to magnetoplumbite². NaV₆O₁₁, crystallizes in P6₃/mmc (a=5.7123(1), c=13.0974 (4) Å, Z=2) at room temperature², shows magnetic phase transitions at 245 K and 64.2 K³. Above 245 K, NaV₆O₁₁ shows metallic conductivity and its magnetic susceptibility obeys Curie-Weiss law. Between 64.2 K and 245 K, NaV₆O₁₁ shows metallic conductivity parallel to [001] but behaves as a semiconductor perpendicular to [001], and its magnetic susceptibility does not obey Curie-Weiss law. Below 64.2 K, it shows metallic conductivity
both parallel and perpendicular to [001], and exhibits spontaneous magnetization with the easy axis of magnetization parallel to [001]^{4).} 

SrV_{6}O_{11}^{5)} crystallizes in P6_{3}/mmc (a=5.7716(1), c=13.0793(5) Å, Z=2) at room temperature also\(^2\), shows magnetic phase transitions at 320 K, around 70 K, and around 35 K\(^6\). The transitions at 320 K and around 70 K correspond to those at 245 K and 64.2 K in NaV_{6}O_{11}, respectively. Between 35 K and 70 K, SrV_{6}O_{11} behaves as an insulator perpendicular to [001], and shows spontaneous magnetization with the easy axis of magnetization parallel to [001]. It shows metamagnetic behavior below 35 K\(^6\).

Magnetoplumbite-type ferrites, BaFe_{12}O_{19} and LaFe_{12}O_{19} (hexagonal, P6\(_{3}/mmc\)) are formed by alternate stacking of spinel and R blocks. AV_{6}O_{11} (A=Na, Sr) phases consist exclusively of the R block. There are three V sites in AV_{6}O_{11}. That is, V(1) octahedra form edge-shared networks perpendicular to [001]; two V(2) octahedra adjoin each other across a mirror plane perpendicular to [001] and form a face-shared dimer; V(3) on the mirror plane is a trigonal bi-pyramidal site\(^2,5\).

To our best knowledge, there has been no ferromagnetic substance, except for AV_{6}O_{11} series, whose spontaneous magnetization is attributed exclusively to vanadium atom (or ion). In this work, crystal structures of NaV_{6}O_{11} and SrV_{6}O_{11} at several temperatures were studied by both neutron and X-ray diffraction, to answer the question whether or not magnetic phase transitions of AV_{6}O_{11} compounds are accompanied by structural phase transitions.

**EXPERIMENT**

NaV_{6}O_{11} single crystal specimen was prepared by heating a mixture of NaVO_{3} and V_{2}O_{3}\(^2,5\). NaV_{6}O_{11} powder were obtained from a mixture of NaVO_{3}, V_{2}O_{3}, and V_{2}O_{5}\(^3\). SrV_{6}O_{11} powder were synthesized from a mixture of Sr_{2}V_{2}O_{7} and V_{2}O_{3}\(^5\).

Structure of NaV_{6}O_{11} at 200 K was analyzed using X-ray single crystal diffraction data collected at NIRIM. Specimen size 0.20×0.17×0.08 mm (along [410], [230] and [001], respectively). Enraf-Nonius CAD4 diffractometer, graphite-monochromatized MoK\(_\alpha\), temperature was controlled by blowing cold nitrogen gas, intensity collection by \(\omega-\theta\) scan with \(\Delta\omega=(0.8+0.35\times\tan \theta)\), \((\sin\theta/\lambda)<0.9949, \,(0\leq h\leq 9, \,0\leq k\leq 9, \,0\leq l\leq 25, \,|h|\leq|k|)\) and \((-9\leq h\leq 0, \,-9\leq k\leq 0, \,-25\leq l\leq 0, \,|h|\leq|k|)\) 1258 reflections measured, 39 unobserved, 1217 reflections with \(I>1.5\sigma(I)\), decrease of intensity within 0.1% during the total exposure time 102.1 hr., absorption correction were applied. Structure refined by least-squares method based on \(F\), anisotropic thermal parameters, atomic scattering factors \((f=f_0+\Delta f+i\Delta f)\) for neutral atoms\(^7\). Computer programs in SDP\(^8\).

Neutron powder diffraction data were collected at several temperatures on the HRPD angle-dispersive type diffractometer installed at the JRR-3 reactor at JAERI\(^9\). The incident neutron beam was monochromatized to give a wavelength of 1.823 Å using the 331 reflection of Ge. The HRPD has a bank of 64 counters placed in 2.5° intervals and Söller collimators of
6° divergence. A scan moves each one of the multicontrolers at a step width of 0.05° over a relatively small portion of the whole scan range. Samples were contained in a cylindrical vanadium cell, which was rotated on its axis during data collection. X-ray powder diffraction data were collected at several temperatures on a MAC Science diffractometer at NCLI with CuKα radiation and graphite-monochromator on the counter side. To minimize preferred orientation, a specimen was dispersed in an acetone solution of a cellulose resin, and the solid obtained by evaporation was ground to a powder. Samples were mounted on a copper holder and cooled by a He gas refrigerator. The sample holder was covered by a thermal shroud to make the temperature gradient minimal. Both neutron diffraction data and X-ray diffraction data were analyzed by the Rietveld method with Rietan10).

RESULTS AND DISCUSSION

X-ray single crystal diffraction data at 200 K showed that NaV₆O₁₁ crystallizes in hexagonal and its possible space groups are P6₃/mmc, P6₂c, or P6₃mc. These groups were examined using 1217 reflections with \( h \geq 1.5 \sigma(h) \). Results are listed on Table I. It shows that P6₃mc models, which lack center of symmetry, are superior to the others, and that model C is slightly better than model D. That is, the magnetic phase transition at 245 K is accompanied by the structural phase transition, from P6₃/mmc to P6₃mc (model C). Consequently, the V(2) at (0,0,1/4+z) is no longer equivalent to adjacent V(2) at (0,0,1/4–z) below 245 K (Fig. I and Table II). Present result rejects the P6₂c model claimed by De Roy et al.¹ for NaV₆O₁₁ at room temperature.

Neutron powder diffraction data on NaV₆O₁₁ at 30 K showed that each \( h00 \) diffraction

<table>
<thead>
<tr>
<th>space group</th>
<th>model</th>
<th>reflection</th>
<th>parameter</th>
<th>( R )</th>
<th>( R_w )</th>
<th>( \Delta \rho_{\text{max}}/e\text{Å}^{-1} )</th>
<th>( \Delta \rho_{\text{min}}/e\text{Å}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P6₃/mmc</td>
<td>1217</td>
<td>24(^a)</td>
<td>0.093</td>
<td>0.178</td>
<td>+18.15</td>
<td>-20.94</td>
<td></td>
</tr>
<tr>
<td>P6₃/mmc</td>
<td>613(^b)</td>
<td>24(^a)</td>
<td>0.093</td>
<td>0.177</td>
<td>+9.05</td>
<td>-10.41</td>
<td></td>
</tr>
<tr>
<td>P6₂c</td>
<td>A</td>
<td>1217</td>
<td>24(^c)</td>
<td>0.086</td>
<td>0.171</td>
<td>+15.45</td>
<td>-22.66</td>
</tr>
<tr>
<td>P6₂c</td>
<td>B(^d)</td>
<td>1217</td>
<td>24(^c)</td>
<td>0.086</td>
<td>0.171</td>
<td>+15.39</td>
<td>-22.70</td>
</tr>
<tr>
<td>P6₃mc</td>
<td>C</td>
<td>1217</td>
<td>43</td>
<td>0.023</td>
<td>0.040</td>
<td>+2.05</td>
<td>-2.56</td>
</tr>
<tr>
<td>P6₃mc</td>
<td>D(^e)</td>
<td>1217</td>
<td>43</td>
<td>0.023</td>
<td>0.041</td>
<td>+2.06</td>
<td>-2.57</td>
</tr>
</tbody>
</table>

\(^{a}\) anisotropic thermal parameters were not applicable to O(2), because isotropic thermal parameter of O(2) was negative.

\(^{b}\) \( F(hk0) \) and \( F(hkl) \) are averaged.

\(^{c}\) anisotropic thermal parameters were applicable to neither O(1) nor O(2).

\(^{d}\) mirror image of model A, but model A and model B are not enantiomeric.

\(^{e}\) mirror image of model C, but model C and model D are not enantiomeric.
Fig. 1 Structural phase transition of NaV$_6$O$_{11}$. Upper figures indicate [110] sectional views. Lower figures show [001] sectional views with z=0. Large open circles, large shaded circles, and small circles, indicate oxygen, sodium, and vanadium atoms, respectively. Broken lines denote mirror planes perpendicular to [001]. Vertical lines denote 3-fold axes.

Table II Summary of phase transitions in NaV$_6$O$_{11}$.

<table>
<thead>
<tr>
<th>temp.</th>
<th>magnetism</th>
<th>conductivity</th>
<th>cryst. system</th>
<th>space gr.</th>
<th>Wyckoff's notation</th>
<th>V(1)</th>
<th>V(2)</th>
<th>V(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>245 K</td>
<td>Curie-Weiss paramag. metallic (// and \perp)</td>
<td>hexagonal</td>
<td>P6$_3$/mmc</td>
<td>6g</td>
<td>4e</td>
<td>2d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64.2 K</td>
<td>paramag. metallic (//) hexagonal P6$_3$mc 6c 2a+2a 2b semiconductor (\perp)</td>
<td>spontaneous metallic orthorhombic Cmc2$_1$ 4a+8b 4a+4a 4a</td>
<td>magnetization (//) (// and \perp)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\:// parallel to [001], \perp: perpendicular to [001].
splits into 2 peaks, while 00l diffractions do not split (Fig. 2). The diffraction pattern was successfully indexed applying orthorhombic symmetry, where \( \vec{a}_0 = \vec{a}_h + b_h \), \( \vec{b}_0 = - \vec{a}_h + b_h \), and \( \vec{c}_0 = \vec{c}_h \). And the pattern satisfied extinction rules, \( l \neq \text{odd} \) if \( k = 0 \) and \( h + k \neq \text{odd} \) for all reflections. Consequently, possible space groups are Cmcm, C2cm, or Cmc2_1. The space groups, Cmcm, C2cm, and Cmc2_1 are the maximal orthorhombic subgroups of P6_3/mmc, P6_2c, and P6_3mc, respectively\(^{11} \). Therefore, we prefer Cmc2_1, though Cmc2_1 lacks center of symmetry and it is impossible to compare intensities of Bijvoet pair from powder diffraction data. Rietveld analyses of both neutron and X-ray diffraction data were successful on the basis of the Cmc2_1 model. Neutron diffraction profile is shown in Fig. 3a. The magnetic phase transition at 64.2 K is accompanied by the structural phase transition, from P6_3mc to Cmc2_1. Consequently, not only the V(2) but also the V(1) splits into two sites below 64.2 K (Fig. 1 and Table II).

![Fig. 2](image)

**Fig. 2** Neutron diffraction profiles of NaV\(_6\)O\(_{11}\) at 30 K (circle) and 106.5 K (triangle). Figures a and b indicate 006\(_h\) and 220\(_h\) diffractions, respectively.

SrV\(_6\)O\(_{11}\) is isostructural with NaV\(_6\)O\(_{11}\) at room temperature\(^2 \) and shows magnetic phase transitions at 320 K, around 70 K, and around 35 K\(^6 \). Neutron powder diffraction data were collected at 22 K, 55 K, 100 K, room temperature, and 373 K. The diffraction profile at 22 K is shown in Fig. 3b. Contrary to NaV\(_6\)O\(_{11}\), SrV\(_6\)O\(_{11}\) maintained hexagonal symmetry from 22 K to 373 K and no structural phase transition was detected.
Fig. 3  Rietveld refinement profiles of (a) NaV₆O₁₁ at 30 K and (b) SrV₆O₁₁ at 22 K. Structural parameters of NaV₆O₁₁ and SrV₆O₁₁ were refined employing space groups, Cmc₂₁ and P6₃/mmc, respectively.
REFERENCES

NEUTRON SCATTERING STUDY
OF HEISENBERG-LIKE SPIN GLASS \( \text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3 \)

Hazuki KAWANO, Hideki YOSHIZAWA and *Atsuko ITO

Institute for Solid State Physics, University of Tokyo
Roppongi, Minato-ku, Tokyo, 106, Japan

*Faculty of Science, Ochanomizu University
Otsuka 2-1-1, Bunkyo-ku, Tokyo, 112, Japan

ABSTRACT

A mixed compound \( \text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3 \) with two competitions of exchange interactions and of weak anisotropies was studied by neutron scattering experiments, and its \( x-T \) phase diagram was established. In addition to the spin-glass (SG) and re-entrant spin-glass (RSG) behaviors, two types of spin axis rotation were observed. One is a spin axis rotation due to the competition of anisotropies, the other is a new type of the spin axis rotation in which spins rotate from the spin easy axis against the anisotropy. We interpret that the latter rotation occurs by the competition of the subtle energy balance between the exchange frustration, the singleion anisotropy and the dipole interaction. From the magnetization measurement, we find that a weak single-ion anisotropy causes the successive SG transitions in the \( \text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3 \) system. By the profile analysis of quasi-elastic scattering, we find that there appears the diffuse scattering which cannot be explained by single Lorentzian below the lower SG transition temperature.

INTRODUCTION

There are a number of investigations on Heisenberg spin glass (SG) properties for almost two decades. Most of samples studied are polycrystalline samples of magnetic diluted alloys. In order to study the Heisenberg SG behavior more precisely, a non-diluted system and its single crystal sample would be desirable. A family of mixed compound system \( \text{Fe}_x\text{Mn}_{1-x}\text{TiO}_3 \) and \( \text{Co}_x\text{Mn}_{1-x}\text{TiO}_3 \) is one of the examples of non-dilute SG system[1]. From this family, we choose a \( \text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3 \) system to study the Heisenberg SG behavior. In addition to the competition of exchange interactions, however, it possesses a competition of the spin anisotropies, and yield a complicated phase diagram. We investigated all the concentration region of the \( \text{Ni}_x\text{Mn}_{1-x}\text{TiO}_3 \) by neutron scattering and DC susceptibility, and established \( x-T \) phase diagram[2][3]. In this paper we report the behaviors observed in the neutron scattering measurements, including the novel successive spin axis rotation and the successive SG transitions.

NEUTRON EXPERIMENTS

Single crystals were grown by the Floating-Zone method. The concentration gradient of each sample was within 0.0003/mm and the mosaic of the samples was less than 10°. Neutron
scattering experiments were performed on a triple axis spectrometer ISSP-4G installed in JRR-3M at JEARI, Tokai. Incident neutron with $k_i = 2.57$ or $2.67 A^{-1}$ was selected by pyrolytic graphite (PG) (002) reflection, and a PG filter was set in front of the monochromator to suppress higher energy neutrons. Each sample was mounted so as to give the (h0l) scattering plane. The spectrometer was operated in the double axis configuration, and we measured the temperature dependence of Bragg and diffuse scattering intensity with a combination of collimators of 40'-40'. For the SG sample $x=0.42$, the temperature dependence of the transverse profile was measured around the NiTiO$_3$-type Bragg point (0, 0, 1.5) with collimators of 20'-20'-20'. In this case, transverse, longitudinal and vertical resolutions (FWHM) of the spectrometer at the (0,0,1.5) reciprocal lattice point were 0.00225 (r.l.u.), 0.0380 (r.l.u.) and 0.10 (Å$^{-1}$), respectively.

RESULTS

(A) MAGNETIC STRUCTURE

In this section we report two spin axis rotations observed in the MnTiO$_3$ type AF region ($x=0.25, 0.38$).

(i) spin axis rotation (1) : $x=0.25$

The temperature dependences of Bragg intensity and diffuse intensity at around the MnTiO$_3$ type Bragg point (0, 0, 3) and (1, 0, -1) are shown in Fig.1(a) and (b), respectively. The Bragg intensity of (1, 0, -1) grows rapidly below $T_N = 37.0\pm 0.5 K$, indicating the MnTiO$_3$ type long range order (LRO) was established. With further lowering the temperature, the Bragg intensity slightly decreases around 20K, but turns to increase below 15K. On the other hands, the temperature dependence of the Bragg intensity at (0, 0, 3) has no anomaly at $T_N$ and appears at the lower temperature $T_{R(1)S} = 19.0\pm 0.5 K$ and increases monotonically at lower temperatures. The diffuse intensity at (0.957, 0, -1) exhibits a peak of the critical scattering at $T_N$, while that at (0, 0, 2.86) exhibits peaks at $T_N$ and $T_{R(1)S}$, respectively. Both increase rapidly at low temperatures. The different temperature dependence of the Bragg intensity of (0, 0, 3) and (1, 0, -1) indicates a rotation of the spin axis. As shown in Fig.1(c), the MnTiO$_3$ type LRO with the spin axis parallel to the c-axis is established first at $T_N$, then it starts to rotate towards the c-plane at $T_{R(1)S}$, and finishes the rotation at $T_{R(1)S} = 15.5 K$ with the final moments parallel to the c-plane.

Fig.1(a)(b) Temperature dependence of the Bragg and diffuse intensity at around (0,0,3) and (1.0,-1), respectively.

(c) Temperature dependence of the moments parallel to the c-axis, $M_C^2$, and that to the a-axis, $M_a^2$, respectively.

— 221 —
(ii) spin axis rotation (2): $x = 0.38$

The temperature dependences of Bragg intensity and diffuse intensity for the $x = 0.38$ sample are shown in Fig. 2(a) and (b), respectively. The Bragg intensity of (0, 0, 3) appears at $T_N \approx 17.8 \pm 0.3 K$. With lowering the temperature, the Bragg intensity increases monotonically, shows a round peak around 12K and then turns to decrease until becoming the back ground counts. The Bragg intensity of (1, 0, 2) also appears at $T_N$. Its temperature dependence is the same with that of (0, 0, 3) until about 7K, then it turns to increase. The temperature dependences of diffuse intensity at (1, 0, 2.85) and (1, 0, 1.85) were observed from the higher temperature than $T_N$. They exhibit cusps at lower temperature $7.5 \pm 0.5 K$. As is the case of the $x = 0.25$ sample, the difference of the temperature dependence of the Bragg intensity between at (0, 0, 3) and (1, 0, 2) indicates a spin axis rotation. The result of the analysis for this data is depicted in Fig. 2(c). From this picture we find that in this sample the MnTiO$_3$ type LRO with the spin axis parallel to the c-plane sets in at $T_N$, its spin axis starts to rotate toward the c-axis at $T_{R(25)} = 8.5 \pm 0.5 K$ and the rotation stops at $T_{R(25)} = 6.0 \pm 0.5 K$ with the moments parallel to the c-axis. It should be noted that this spin axis rotation takes place by the expense of the single-ion anisotropy energy, in contrary to the rotation observed in the $x = 0.25$ sample. This type spin axis rotation has not observed until this work. Our interpretation will be discussed in the latter section "Phase diagram & discussion".

By the magnetization measurement, we find that the $x = 0.38$ sample exhibits a RSG transition at $9.5 \pm 0.5 K$. The intensity of the magnetic Bragg scattering is also observed below the RSG transition temperature. This means that the RSG phase of this system is a mixed phase, consisting of the SG ordering and the MnTiO$_3$ type LRO.

Fig. 2(a)(b) Temperature dependence of the Bragg and diffuse intensity at around (0,0,3) and (1,0,2) for the RSG sample of $x = 0.38$.

(c) Temperature dependence of the moments parallel to the c-axis, $M_c^2$, and that to the a-axis, $M_a^2$, respectively.
(B) PROFILE ANALYSIS

In the SG and RSG samples, the temperature dependence of irreversibility between field-cooled and zero-field-cooled magnetization exhibits two anomaly, suggesting the successive SG transitions. In order to obtain the information on the successive SG transitions by neutron scattering measurements, quasielastic scattering measurements were performed. The results of the x=0.42 SG sample are reported below.

By the magnetization measurement of the x=0.42 sample, the moment parallel to the easy axis freeze at $T_{SG}^{1/2}=9.5\pm0.5$K and the SG freezing of the transverse moment takes place at $T_{SG}^{3}=6.0\pm0.5$K.

The temperature dependence of the quasi-elastic neutron scattering profiles is shown in Fig.3(a). With decreasing the temperature, the inverse geometrical correlation length $\kappa(=1/\xi)$ decreases, and the intensity in a small q region increases accordingly. A sharp Bragg-like peak observed at q=0 may be caused by the higher order contamination or by the double scattering of the intense diffuse scattering. First we analyzed the profile data by assuming that the magnetic scattering consists of the Lorentzian term and necessary back ground terms. However, agreement of the profile becomes progressively worse at low temperatures because of rapid increase of the diffuse scattering in the small q region. In order to account for the deviation from the q^2 dependence, we tentatively added the squared-Lorentzian term to the cross section as shown in eq.(1). This form was chosen to describe disordered frozen states expected for the SG phase in an analogy of the random field problem[4].

$$S(q) = \frac{A}{\kappa^2 + q^2} + \frac{B}{(\xi^2 + q^2)^2} + G\delta(0) + B.G.$$  

Fig.3. (a) Temperature dependence of the quasi-elastic neutron scattering profiles. (b) Temperature dependence of Lorentzian $A/\kappa^2$ and squared-Lorentzian $B/\kappa^4$ at q = 0

The temperature dependence of the cross section $S(q=0)$ is shown in Fig.3(b), where the contribution of the Lorentzian $A/\kappa^2$ and that of squared-Lorentzian $B/\kappa^4$ are separately depicted. We find that on lowering the temperature, the diffuse scattering gradually increases and the intensity of the Lorentzian component becomes significant below $T_{SG}^{1/2}$. On further lowering the temperature, the deviation from the Lorentzian becomes non-negligible. Below $T_{SG}^{1/2}$, the squared-Lorentzian term steeply increases, although a substantial fraction of the Lorentzian contribution still remains. The temperature at a rapid increase of Lorentzian component as well as the temperature where the Lorentzian squared component appears are in excellent agreement with the SG successive transition temperatures $T_{SG}^{1/2}$ and $T_{SG}^{3}$ which are determined by the magnetization measurements.
PHASE DIAGRAM AND DISCUSSION

The magnetic x-T phase diagram of Ni$_x$Mn$_{1-x}$TiO$_3$ is shown in Fig.4. In this system, SG and RSG behaviors were observed. The RSG phase of the system is found to be the mixed phase of the coexistence of MnTiO$_3$ type or NiTiO$_3$ type LRO and the SG ordering.

In the MnTiO$_3$ AF phase, two kinds of spin axis rotation were observed. One is a rotation from parallel to perpendicular to the c axis, and the other is a rotation from perpendicular to parallel to the c axis.

![Phase Diagram](image)

**Fig.4**
The magnetic phase diagram of Ni$_x$Mn$_{1-x}$TiO$_3$ system.
A hatched region indicates the region where the spin axis rotates.

The starting temperature of the rotation $T_{K(1,5)}$, increases with the higher concentration of Ni. This indicates that the spin axis rotation is due to the competition between the dipole interaction and the single-ion anisotropy of Ni$^{2+}$. In contrast, the second rotation observed in x=0.38 sample is very unusual, and we interpret it as described below. The MnTiO$_3$ type LRO with the moment parallel to the c plane is first established at $T_N$. With decreasing the temperature, the moment becomes larger, and the frustration due to the competition among exchange interactions increases. Then with further lowering the temperature, an energy loss by the frustration of exchange interactions exceeds the energy gain by the single-ion anisotropy so that the local moments can point any direction against the easy axis. In other words, the local moments will realign the local spin axis to reduce the exchange frustration. The dipole interaction favors the moments to align along the c axis for the MnTiO$_3$ type AF structure.

In the present study, two successive SG transitions associated with the longitudinal and transverse components were observed in the Heisenberg-like SG sample Ni$_{0.42}$Mn$_{0.58}$TiO$_3$. This phenomenon is naturally explained by taking account of the effect of the single-ion anisotropy. According to a mean field theory by Cragg and Sherrington[5] and by Roberts and Bray[6], a weak anisotropy splits the SG transition into two transitions. In a Heisenberg-like SG system with a weak single-ion anisotropy, regardless of the type of the spin anisotropy D > 0 or D < 0, the components parallel to the anisotropy freeze first and the perpendicular component freezes successively. We interpret that a weak planar anisotropy in the Ni$_{0.42}$Mn$_{0.58}$TiO$_3$ sample causes a SG freezing of the in-plane component first at $T_{SG}^/$, and then it causes the freezing of the
remaining component parallel to the c-axis at the lower transition temperature $T_{SG}$. Note that the c-axis component maintains the freedom of fluctuations in the intermediate phase for $T_{SG} < T < T_{SG}$, but all components are frozen below $T_{SG}$. In the present neutron scattering experiments the deviation of the scattering function from the Lorentzian is observed only in the totally frozen SG state. We emphasize here that the change of the features of the diffuse scattering is consistent with the magnetization measurements and the combined results strongly support two successive SG transitions in the Heisenberg-like SG system with a weak planar anisotropy.

In $\text{Ni}_{0.75}\text{Mn}_{0.25}\text{TiO}_3$ system, we observed a variety of magnetic phases, including the new successive spin axis rotation and the successive SG (RSG) transition. We hope that this system provides useful information for studies on a magnetically random system.

Reference

SPIN DYNAMICS OF CONCENTRATED METALLIC SPIN GLASSES

Kiyoichiro MOTOYA and Satoshi KUBOTA

Department of Physics, Faculty of Science, Saitama University, Urawa, 338 Japan

ABSTRACT

Neutron scattering experiments have been made on two kinds of reentrant spin-glass alloys, Fe_{65}(Ni_{0.866}Mn_{0.134})_{35} and Cu_{2}(Mn_{0.70}Ti_{0.30})Al. The former can be classified as an itinerant electron magnet. The latter is a typical member of localized moment magnets. For both systems, magnetic diffuse scattering intensity increases as the system is cooled toward the spin-glass freezing temperature even in the ferromagnetic phase. However, the magnetic correlation length in the Fe_{65}(Ni_{0.866}Mn_{0.134})_{35} is considerably larger than that in the Cu_{2}(Mn_{0.70}Ti_{0.30})Al. In the Fe_{65}(Ni_{0.866}Mn_{0.134})_{35}, spin-wave excitations have been observed in the spin-glass phase as well as in the ferromagnetic phase. Spin-wave stiffness constant does not change appreciably at the spin-glass freezing temperature.

INTRODUCTION

Macroscopic magnetic properties and magnetic phase diagrams of concentrated spin-glasses show rather universal characteristics among many materials including metallic and insulating, crystalline and amorphous solids. However, the characters of the ferromagnetic (antiferromagnetic) and the spin-glass phases of these re-entrant spin-glasses (RSG’s) have not yet been fully clarified. Moreover, a question "Whether there are true phase transitions or not in RSG’s?" has not yet been unambiguously answered. To make clear these points, neutron scattering experiments in various RSG materials have been made. In the ferromagnetic phase, characteristics of the spin-wave dispersion and energy width are quite similar to the cases for normal ferromagnets. However, there are marked differences among materials in the temperature variation behavior of the spin-wave stiffness constant and the spin-wave intensity. The spin-wave stiffness constant $D$ increases as the temperature decreases below $\sim$70K ($\sim1.8T_{S.G.}$) in Ni_{0.784}Mn_{0.216} alloy. On the other hand, in other RSG alloys such as Fe_{0.26}Cr_{0.74}, Fe_{0.70}Al_{0.30} and amorphous (Fe_{1.5},Mn_{0.75})P_{16}B_{6}Al_{3}, $D$ decreases gradually in the ferromagnetic phase as the temperature decreases toward the RSG phase. In the Ni_{0.784}Mn_{0.216} and the Fe_{0.26}Cr_{0.74} alloys, spin wave intensity (corrected for thermal factor) increases at low temperature whereas in the Fe_{0.70}Al_{0.30} alloy it decreases at low temperature. Moreover at the lowest temperature in the RSG phase, spin-wave excitations are observed for the Ni_{0.784}Mn_{0.216} and the Fe_{0.26}Cr_{0.74} alloys. On the other hand, for the Fe_{0.70}Al_{0.30} alloy, no propagating excitations have been observed at the lowest temperature.

In order to clarify the nature of each magnetic phase and phase transition properties and especially to make clear the origin of the wide variety in spin dynamical properties, much experimental studies of spin dynamics of suitable materials are needed. Especially, experiments on materials chosen from a viewpoint of itinerant electron magnetism might be
very interesting to probe the relation between spin-glass characteristics and the itinerant character of magnetic electrons, on which much attention has not been paid so far.

We made elastic and inelastic neutron scattering experiments of a pseudo-binary alloy Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$. We also present a result of elastic neutron scattering experiment on Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al. The former system is a mixture of a ferromagnetic Fe$_{65}$Ni$_{35}$ Invar alloy and an antiferromagnetic Fe$_{65}$Mn$_{35}$ alloy. The Fe$_{65}$Ni$_{35}$ Invar alloy has been extensively studied from a viewpoint of itinerant electron magnetism. The Fe-Mn alloy system has been regarded as an itinerant electron antiferromagnet. Therefore the system can be classified as an example of itinerant electron magnetic materials. The latter system, in which magnetic Mn atoms are diluted with Ti atoms in a Heusler alloy, can be regarded as a typical example of localized moment system of metallic materials.

The magnetic property of the Fe$_{65}$(Ni$_{1-x}$Mn$_x$)$_{35}$ system was first investigated by Shiga before the discovery of spin-glass. It was found that the alloy is an antiferromagnet in the composition range 0.3\(<x<1.0$, and a ferromagnet for 0\(<x<0.3$. Shiga et al. re-investigated the magnetic properties of the Fe$_{65}$(Ni$_{1-x}$Mn$_x$)$_{35}$ system from a viewpoint of a concentrated spin-glass. A magnetic phase diagram has been determined by means of ac and low field dc susceptibility measurements (Fig.1 (a)). Re-entrant spin-glass phase was found for x\(<0.2$.

The magnetic phase diagram of the Cu$_2$(Mn$_{1-x}$Ti$_x$)Al system was determined by the present authors by means of low field magnetization measurements. Phase diagrams of the Cu$_2$(Mn$_{1-x}$Ti$_x$)Al system is shown in Fig. 1 (b). Arrows in the figure show the compositions of the present samples.

---

**EXPERIMENTAL PROCEDURE**

A single crystal of the Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ alloy was grown by the Bridgman technique. The crystal has disordered face centered cubic structure. The size of the sample cut for the neutron scattering measurements is \(8\text{mm} \times 9\text{mm} \times 10\text{mm}\). The mosaic spread of the sample is \(1^\circ\). A single crystal of Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al alloy was also grown by the Bridgman method. The size of the single crystal is \(15\text{mm} \times 20\text{mm}\). Magnetic susceptibility measurements were made utilizing a SQUID magnetometer (Quantum Design model MPMS). Temperature variation of magnetic susceptibility was measured after the sample
was cooled in zero applied field to the lowest temperature then switched on the field (zero field cool, ZFC) or cooled in the same field as applied for the measurement (field cool, FC).

Neutron scattering measurements were made using spectrometers installed at the reactors of JAERI-Tokai. Most of the inelastic scattering measurements were made utilizing a new "4G" triple axis spectrometer installed at a newly constructed reactor JRR-3M. Elastic scattering patterns were obtained utilizing either a triple axis spectrometer installed at JRR-2 or the "4G" triple axis spectrometer with an analyzer angle fixed to the elastic position. For both spectrometers, pyrolytic graphite crystals were used for a monochromator and an analyzer. A pyrolytic graphite filter was used to eliminate higher energy neutrons. Inelastic scattering measurements were made in constant-Q scan mode. A typical instrumental energy resolution of $2\Gamma_{\text{FWHM}} = 0.46\text{meV}$ (full width at half maximum, FWHM) was obtained with the incident neutron energy of $14.8\text{meV}$ and the horizontal beam collimation of $20' - 20' - 20' - 20'$.

RESULTS AND ANALYSIS

Temperature variation of magnetic susceptibility for Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ is shown in Fig.2(a). Measurements were made under the field of 100 Oe. Solid and open symbols correspond to the zero field cool (ZFC) and the field cool (FC) measurements, respectively.

![Fig.2 Temperature dependence of magnetic susceptibility for (a) Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ and (b) Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al. Measurements were made under the field of 10 Oe. Solid and open symbols correspond to the zero field cool and field cool measurements, respectively.](image)

Below $T_{\text{S.G.}} = 30K$, the ZFC susceptibility value increases with increasing temperature. Nearly temperature independent susceptibility is observed between $T_{\text{S.G.}}$ and $T_C = 300K$, which is a result of the cut-off by a demagnetization field in the ferromagnetic phase. A large field hysteresis effect is observed below $T_{\text{S.G.}}$. These behaviors are characteristics for RSG materials. The field hysteresis persists up to $T = T_C$. The origin of the hysteresis above $T_{\text{S.G.}}$ has not been clarified. The results show that Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ transforms from a paramagnetic phase to a ferromagnetic phase at $T_C = 300K$, then enters a spin-glass phase at $T_{\text{S.G.}} = 30K$. Temperature dependence of magnetic susceptibility for Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al

---

\[ \text{---228---} \]
alloy under the field of 10Oe is shown in Fig. 1(b). The result, which is quite similar to the one for Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$, shows that the Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al alloy transforms from a paramagnetic phase to a ferromagnetic phase at $T_C=270$K, then enters a spin-glass phase at $T_{SG}=50$K.

Elastic neutron scattering pattern for the Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ alloy is shown in Fig. 3 (a). Scans were made along the $(\xi,\xi,\xi)$ direction across the (111) Bragg point. The scattering pattern is composed by a resolution-limited Bragg peak and tails spread both sides of the Bragg peak. The Bragg peak is a superposition of nuclear and magnetic scattering intensities. A quantitative analysis of the scattering pattern was made with the assumption that the pattern is composed by a Bragg peak, a diffuse scattering component and a constant background (B.G.).

![Graphs showing neutron scattering intensities](image)

Fig. 3. Neutron scattering intensities as a function of momentum transfer around the (111) Bragg peak for (a) Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ and (b) Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al alloys. Curves represent the results of fitting described in the text.

The Bragg peak is represented by a Gaussian function (GAU) determined by a resolution function of the spectrometer. The diffuse scattering part was found to be well traced by a sum of a Lorentzian (LOR) and a squared Lorentzian (SQL) functions. The amplitude and the width of each function and the background intensity were determined by least square fitting to the observed pattern. Elastic neutron scattering pattern for the Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al alloy is shown in Fig. 3 (b). The pattern, which is qualitatively same as the one for the Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ alloy, is analyzed following the same procedure.

Temperature dependence of integrated intensities and line widths of the LOR and the SQL components for the two samples are shown in Fig. 4. The results show that the major contribution to the diffuse scattering is represented by the SQL component for each system. Amplitudes of both the LOR and the SQL components increase with decreasing temperature. The line width of neither the LOR nor the SQL component changes appreciably with temperature for Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$. For Cu$_2$(Mn$_{0.70}$Ti$_{0.30}$)Al, line width for each component increases slightly at low temperature and the width of SQL is considerably wider than the one of Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$.
Inelastic neutron scattering spectra of the alloy Fe\(_{65}(\text{Ni}_{0.886}\text{Mn}_{0.114})_{35}\) at two representative temperatures are shown in Fig.5. At \(T=8\text{K}\), where the spin-glass freezing has been indicated by susceptibility measurements, the scattering patterns do not change essentially from those in the ferromagnetic phase \((T=200\text{K})\).

Temperature dependence of the spin-wave stiffness constant and the spin-wave gap energy for the alloy Fe\(_{65}(\text{Ni}_{0.886}\text{Mn}_{0.114})_{35}\) are shown in Fig.6. The spin-wave stiffness constant increases slightly as temperature decreases below \(T=50\text{K}\). The spin-wave gap energy \(\Delta\) does not change within the experimental error.

Temperature dependence of the spin-wave line width and the intensity \(A_S\) for the Fe\(_{65}(\text{Ni}_{0.886}\text{Mn}_{0.114})_{35}\) alloy are shown in Fig.7. The width at \(q=0.243\text{ Å}^{-1}\) increases appreciably with decreasing temperature. It should be noted that the spin-wave intensity \(A_S\) increases significantly with decreasing temperature.

**Fig.4.** Temperature dependence of the amplitude and line width of Lorentzian (LOR) and squared Lorentzian (SQL) scattering components for (a) Fe\(_{65}(\text{Ni}_{0.886}\text{Mn}_{0.114})_{35}\) and (b) Cu\(_2(\text{Mn}_{0.75}\text{Tl}_{0.30})\)Al alloys.

**Fig.5.** Inelastic neutron scattering spectra for the Fe\(_{65}(\text{Ni}_{0.886}\text{Mn}_{0.114})_{35}\) alloy measured at (a) \(T=8\text{K}\) (spin glass phase) and at (b) \(T=200\text{K}\) (ferromagnetic phase). Curves represent the least square fitting.
Fig. 6. Temperature dependence of spin-wave stiffness constant $D$ and spin-wave gap energy $\Delta$ of the Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ alloy. Curves are drawn to guide the eye.

Fig. 7. Temperature dependence of spin-wave line width $\Gamma_q$ and spin-wave intensity $A_S$ of the Fe$_{65}$(Ni$_{0.866}$Mn$_{0.134}$)$_{35}$ alloy. Curves are drawn to guide the eye.

DISCUSSION

The elastic neutron scattering experiments have shown that the diffuse scattering intensity starts to increase at the temperature far above $T_S G$ and keep increasing as the sample is cooled all the way down to the lowest temperature for both systems. A remarkable observation in the present system is the presence of two separate components in the diffuse scattering signal. The Lorentzian component is due to the scattering from finite size magnetic clusters. The squared
Lorentzian component can be interpreted as an effect of random fields that destroy the ferromagnetic order. Coexistence of these two components has also been observed in other RSG alloys. For the Fe\(_{0.7}\)Al\(_{0.3}\) alloy, the squared Lorentzian component disappears at low temperature.\(^5\) On the other hand, in the present systems, the intensities of the two components increase quite similarly with decreasing temperature and the temperature variation of the line width of each component is quite small. A remarkable difference between the two systems is the line width of the squared Lorentzian component, which indicates the magnetic correlation length (size of the clusters) for the Fe\(_{65}(\text{Ni}_{0.866}\text{Mn}_{0.134})_{35}\) alloy is about one order of magnitude larger than that of Cu\(_2(\text{Mn}_{0.70}\text{Ti}_{0.30})\)Al.

Spin-wave excitations are clearly observed down to the lowest temperature in the RSG phase of Fe\(_{65}(\text{Ni}_{0.866}\text{Mn}_{0.134})_{35}\). The spin-wave stiffness constant \(D\) slightly increases in the RSG phase. The spin-wave amplitude increases at lower temperatures. These behaviors are the same as those observed in the polycrystalline Ni\(_{0.784}\)Mn\(_{0.216}\) and the amorphous (Fe\(_{0.73}\)Mn\(_{0.27}\))\(_{75}\)P\(_{16}\)B\(_{6}\)Al\(_{3}\) alloys.\(^3,12\) However, in these materials spin-waves have been observed only in much smaller \(q\) region. The existence of spin-waves in the RSG phase has been one of the most controversial points in the spin-glass problem. Spin-wave excitations are observed in some materials and are absent in others. Sometimes the result might be changed by the improvement of instrumental energy resolution.\(^7\) The conclusion might be reversed by the change of the experimental conditions, such as the \(q\) range and the signal-to-noise ratio of the spectrometer. The answer to the question “Does spin-wave excitation exist in this material?” might be changed by the combination of the instrumental conditions and the spin-wave parameters of the material such as the stiffness constant, the energy width and the intensity. Therefore, our goal is to clarify the relation between these spin-wave parameters and the electronic states of the specific material. The origin of apparent differences in spin-wave characteristics between materials might be clarified through the aforementioned study.

In view of the fact that the variety of characteristics in RSG’s is most clearly appeared in dynamical characters, one might be led to the idea that the variety is closely related with the dynamical characteristics of magnetic electrons. In other words, temporal and spatial character of magnetic moments, \(i.e.,\) the spin fluctuation property, plays an important role to the dynamics of spin-glasses. These properties vary widely among metallic materials as has been demonstrated for ferromagnetic and antiferromagnetic materials.

For more than two decades, the importance of proper understanding of spin fluctuation properties has widely been recognized in the field of metallic magnetism. Many theoretical and experimental works have been made to aim the unified understanding of the itinerant electron magnetism.\(^13\) However, in the field of spin-glasses, the aspect of spin statistics or phase transition property has been regarded as the most important and almost the unique problem. Therefore, even in metallic spin-glasses, magnetic moments have been regarded as stable and localized same as the cases of insulators. Difference between metallic and insulating spin-glasses, aside from the range of exchange interactions, has been neglected so far. Recently, we pointed out that proper treatment of magnetic moments taking account of the itinerant character of magnetic electrons is essentially important in the study of concentrated metallic spin glasses.\(^14\)

The present study is a part of work on spin dynamics of spin-glasses undertaken with the aim of unified understanding of RSG problem from a viewpoint of itinerant electron magnetism. Our future plan is to investigate the spin dynamics of other typical materials including the Cu\(_2(\text{Mn}_{X}\text{Ti}_{1-X})\)Al system classified from spin fluctuation point of view.
ACKNOWLEDGMENTS

We thank to Professor H.Yoshizawa and the neutron scattering group of the Institute for Solid State Physics for their excellent design and construction of the "4G" spectrometer. This work was partially supported by a Grant-in-Aid for Scientific research from the Ministry of Education, Science and Culture.

REFERENCES

1) See, for example, K.Binder and A.P.Young: Rev.Mod.Phys. 58 (1986) 801.
ON THE 1 0 0 MAGNETIC DIFFUSE PEAK IN γ-Fe PRECIPITATES IN Cu

Yorihiro TSUNODA and *Robert M. NICKLOW

Faculty of Science, Osaka University, Toyonaka
Osaka 560 Japan

*Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831 U.S.A.

ABSTRACT

The 1 0 0 magnetic diffuse peak of γ-Fe precipitates in Cu is carefully reexamined by neutron diffraction. Distribution of the diffuse peak intensity extends along the [0 1 0] direction. We propose a new magnetic structure of γ-Fe with the c-axis spin component which is compatible with the double-Q spin structure and periodic lattice distortion on the c-plane previously reported.

INTRODUCTION

Iron in the FCC structure (γ-Fe) can be obtained as precipitation particles in a Cu matrix even at room temperature. The magnetic structure of γ-Fe precipitates in Cu was first investigated by Abrahams et al. (1962)[1] by means of neutron diffraction. In addition to the 1 1 0 magnetic peak which corresponds to a longitudinal first-kind antiferromagnetic (L-AF-1) structure, they observed a weak magnetic peak at 0 0 1 reciprocal lattice point. Since the 0 0 1 magnetic peak is prohibited for the L-AF-1 structure, they explained this peak as an inclined spin component from the c-axis as shown in Fig. 1. This structure had been accepted for a long time even after Ehrhart et al. [2] reported the reduction of the crystal symmetry of γ-Fe precipitates at low temperature. However, one of the present author and colleagues studied the structural phase transition of γ-Fe precipitates more carefully using X-ray diffraction[3]. In a low temperature phase, the atomic positions on the c-plane deform periodically and are described

Fig. 1 Magnetic Structure of γ-Fe reported by Abrahams et al.
by a shear wave propagating along the <1 1 0> direction. Along the c-axis, the FCC lattice slightly contracts uniformly by 0.17 %. Since the lattice deformation on the c-plane is far larger (~2.5%) than along the c-axis, local lattice structure is roughly orthorhombic (a' > c > a^*-). This lattice structure is incompatible with the magnetic structure of Fig. 1 and compelled us to reinvestigate the magnetic structure of Y-Fe. In our previous paper, using the peculiar diffraction patterns of the 1 1 0, 1 2 0 and 2 1 0 magnetic peaks, we reported the magnetic structure of Y-Fe precipitates[4]. The results are shown in Fig. 2 together with the periodic lattice distortion. The magnetic moments exist on the c-plane and this is essentially the double-Q wave of the L-AF-1 structure with a periodic spin modulation which reflects the periodic lattice distortion. However, we did not take the 0 0 1 magnetic peak into consideration when we determined this magnetic structure because this peak is rather weak and diffusive and comes from a transverse first kind antiferromagnetic (T-AF-1) structure. In the present paper, the 0 0 1 magnetic peak was carefully reexamined by means of neutron diffraction and we propose a new explanation of the 0 0 1 magnetic diffuse peak without inconsistency with the previous double-Q spin structure on the c-plane.

**MEASUREMENT**

Since Y-Fe particles precipitate coherently to the Cu matrix, if we grow the precipitates in Cu(Fe) single crystal, the crystal axes of all precipitates are parallel to those of the Cu host. Then we can regard all precipitates as a single crystal of Y-Fe for the diffraction experiment. Present specimen is this case. However, when the structural phase transition takes place, all possible variants thermally distribute under the normal condition. In order to simplify the problem, the present measurements were performed under the uniaxial stress of about 300 kg/cm² loaded along the direction perpendicular to the scattering plane. Under this condition, a variant with the c-plane perpendicular to the uniaxial stress
predominantly grows[5]. In the present measurement, about 85% of the precipitates had the c-plane on the scattering plane. This value was estimated from the intensity ratio of the 110 and 210 magnetic peaks.

Mean diameter of the precipitates in the present specimen was about 60 nm which was estimated using the empirical equation related to the thermal treatment and diameter of the precipitates[6].

Neutron scattering measurements were performed at the triple axis spectrometer HQR installed at the thermal guide of the JRR-3, JAERI, Tokai. Some data were taken at the HB-1 triple axis spectrometer at HFIR, ORNL. In order to minimize the higher order contamination of Cu Bragg peaks, thick PG filter was used for both spectrometers.

EXPERIMENTAL DATA

(The index of 001 was used by Abrahams et al. In the present paper, the periodic lattice distortion propagates on the c-plane. Since the c-axis of the predominant variant is perpendicular to the scattering plane, observed diffuse peaks should be indexed as 100 and 010 peaks in the present case.)

Scattering intensity contour map observed at 12 K around the 100 reciprocal point is given in Fig. 3. Diffraction line profile is not the well defined Bragg peak, but the diffusive peak. The intensity distribution is roughly symmetric to the 100 reciprocal point although other magnetic Bragg peaks are extremely asymmetric. These are reasons why we consider this peak separately. One peculiar feature of this diffraction pattern is an extension of the scattering intensity along the [010] direction. Diffuse scattering around the 010 reciprocal point was also studied. Almost the same scattering intensity and diffraction pattern which has the extension axis along the [100] direction was observed.

Temperature variation of the peak intensity was studied. The peak intensity decreases with increasing temperature like an long range order parameter and disappears around the Néel temperature.

MODEL FOR THE 100 DIFFUSE PEAK

The 100 magnetic peak is prohibited for the double-Q wave structure which consists of the [100] and [010]
components with the L-AF-1 type structure on the c-plane. Thus, the observation of the 1 0 0 magnetic peak indicates existence of a component with the T-AF-1 type structure. There are two choices of the T-AF-1 type structure which contributes to the 1 0 0 magnetic peak. The one is that the magnetic moments are parallel to the [0 1 0] axis and the other parallel to the [0 0 1] axis (c-axis). However, in the former, both the L-AF-1 and T-AF-1 type structures are coexistent on the c-plane and we have to assume that not only the direction of spins but the magnitude of the moments are modulated on the c-plane.

It is rather natural to have the c-axis spin component for this lattice structure. This is derived from the analogy to the Y-Mn alloy. The Y-MnNi alloy with an appropriate Ni concentration has an orthorhombic lattice structure ($a > b > c$) and the double-$Q$ wave L-AF-1 spin structure. The spin components are closely related to the lattice spacings, i.e., $m > m > m = 0$. In the case of Y-Fe, the local lattice spacing at the node of the periodic lattice wave has a relation $a > c > a$ as shown in Fig. 2. If we apply the rule for the Y-MnNi alloy to this case, the Y-Fe should have the c-axis spin component at the node of the periodic lattice wave.

We adopt another rule which is common to the 3d-alloys with the first-kind antiferromagnetic structure; the antiferromagnetic (ferromagnetic) coupling is favored in the plane with shorter (longer) n.n. atomic distance.

Under these reasonable assumptions, we obtain the transverse spin configuration on the periodically modulated lattice in Y-Fe precipitates as shown in Fig. 4. In this figure, large circles are the atoms on the c-plane and small circles the lower half c-plane. Open circles indicate the up spins and closed circles down spins. When we run along the [1 0 0] axis, averaged magnetic moments on the successive (1 0 0) planes are zero in a region A but finite in a region B and each (1 0 0) plane couples antiferromagnetically.

---

Fig. 4. A model of the c-axis spin component with the T-AF-1 type structure on the c-plane.
Within a (1 0 0) plane, magnetic moments are periodically modulated along the [0 1 0] direction. Thus the magnetic peaks are expected at 1 0 0 and 1 1b 0 as satellite reflections. Modulation wave vector is estimated to be b ~ 0.025 from the wavelength of the periodic lattice modulation. At the same time, the 0 1 0 and 1b 1 0 reflections are expected around the 0 1 0 reciprocal lattice point.

As for the line width of the diffraction pattern, we have to consider the phase relations between regions A, A' and so on. If the regions A and A' have opposite phase (up spin at A and down spin at A' within a (0 1 0) plane), each region works as an independent magnetic cluster and diffuse peaks are expected due to the limited thickness of each region. The line width is estimated to be Γ' = 0.04 ~ 0.05 for this case. As an actual model, if the phase relation is at random, diffuse peaks at 1 0 0 and 1 1b 0 are expected because in-phase regions extend to the limited area, resulting in the diffusive peaks elongated along the [0 1 0] direction at 1 0 0 and along the [1 0 0] direction at 0 1 0. This is consistent with the diffraction patterns observed around the 1 0 0 and 0 1 0 reciprocal lattice points.

DISCUSSIONS

The 0 0 1 magnetic diffuse peak is commonly observed for the fcc antiferromagnetic system with the L-AF-1 type structure such as FeMn[8], FeNiCr[9], CoMn[10], MnCu[11] and so on. The reason why the T-AF-1 component comes in is not well understood. Ishikawa et al found the anisotropic distribution of the 0 0 1 diffuse peak for γ-FeNiCr alloy[9]. They explained it using a periodically modulated short range spin correlation with the T-AF-1 spin structure. However, the cause of the periodical spin modulation was not given. Since the periodic lattice distortion has not been reported for the FeNiCr system, this case seems to be different from the present γ-Fe precipitates. There is an important difference between γ-Fe precipitates and FeNiCr system. In the former, the 1 0 0 diffuse peak intensity varies with temperature like an order parameter and disappears around the T_N. On the other hand, the 0 0 1 diffuse peak in the latter shows the maximum intensity at the T_N and gradually decreases the intensity above the T_N. Thus the origin of the latter seems to be static or dynamic spin fluctuations due to the randomness of the system.

Recently, in a cubic phase of γ-Fe and γ-FeCo precipitates, a helical spin structure is reported[12]. In this spin structure, the T-AF-1 and L-AF-1 type couplings appear alternately in space along the wave propagation direction, (see Fig. 11 of Ref. [12]) indicating that the T-AF-1 and L-AF-1 spin structures degenerate energetically in the cubic phase. Under the periodic lattice distortion, the degeneracy might be resolved but still energy difference would be small. It is plausible that the T-AF-1 type spin coupling would be stabilized for the c-axis spin component due to the coupling with the lattice distortion.

In conclusion, the 1 0 0 magnetic diffuse peak of γ-Fe
precipitates in Cu was carefully reexamined by means of neutron diffraction. Based on these data, we propose a new explanation of the 1 0 0 diffuse peak using a model of the magnetic structure with the c-axis spin component. This structure is compatible with the basic double-Q spin structure and periodic lattice distortion on the c-plane which were previously reported for the γ-Fe precipitates in Cu.

REFERENCES

SITE PREFERENCE, SUPERCONDUCTIVITY AND MAGNETISM IN
\[ \text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x(\text{Cu}_{1-y}\text{M}_y)_{2-x} \text{O}_8 \] (M = Fe, Co, Ni, Zn, Ga)

Yoji KOIKE, Masahiro KAIWA, Tsuyoshi KAJITANI, Masatsune KATO, Hiromu SUNAGAWA, Takashi NOJII, Yoshitami SAITO, Norio KOBAYASHI, Yukio MORII and Satoru FUNAHASHI

Department of Applied Physics, Faculty of Engineering, Tohoku University, Aramaki Aoba, Aoba-ku, Sendai, 980 Japan

Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai, 980 Japan

†Department of Physics, Tokai Research Establishment, JAERI, Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

Site preference of the partially substituted 3d metal M and superconducting and magnetic properties have been investigated for \[ \text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x(\text{Cu}_{1-y}\text{M}_y)_{2-x} \text{O}_8 \] (M = Fe, Co, Ni, Zn, Ga). It has been found from powder neutron diffraction that Fe atoms occupy the Cu(1) site in the oxygen-free Cu layer, while Co, Ni, Zn and Ga atoms occupy the Cu(2) site in the CuO2 layer. The Cu(1)-site substitution shows a little effect on the superconductivity. The magnetic susceptibility measurements have revealed that there remains antiferromagnetic correlation between Cu spins in the Cu(2) site in the normal state even for the high-\(T_c\) samples of \(x = 0.5\) with \(T_c \approx 80\) K.

INTRODUCTION

The most important feature common to high-\(T_c\) superconductors is that CuO2 layers are included in their crystal structures. The CuO2 layers hold the key to the solution of the question on the appearance of high-\(T_c\) superconductivity. Therefore, it attracts interests to study effects of the partial substitution of 3d metal M (M = Fe, Co, Ni, Zn, Ga) for Cu on the superconductivity. Such works on the Cu-site substitution have been reported for \[ \text{La}_2(\text{Ba},\text{Sr})_1\text{CuO}_4 \] and \[ \text{YBa}_2\text{Cu}_3\text{O}_7 \] (4,5). As for \[ \text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_8 \], no detailed study has been reported.

The crystal structure of \[ \text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_8 \] is characterized by double CuO2 pyramidal layers and the stack of layers along the c-axis is expressed as \[ \text{Y}_x\text{Ca}_{2-x}\text{CuO}_2\text{SrO-PbO-Cu-PbO-SrO-Cu}_2\text{O}_8 \]. There are two kinds of Cu atoms with different valences as in the case of \[ \text{YBa}_2\text{Cu}_3\text{O}_7 \]: One is the monovalent copper, Cu(1), in the oxygen-free Cu layer, and the other is the almost divalent copper, Cu(2), in the CuO2 layer. Cu(1) is nonmagnetic, whereas Cu(2) is magnetic with the spin quantum number \(S \approx 1/2\). Therefore, it is necessary for detailed works on the Cu-site substitution to know which site M atoms occupy. For \(x = 0\), the compound is an insulator developing
antiferromagnetic ordering of Cu\(^{2+}\) spins in the Cu(2) site. When holes are doped in the CuO\(_2\) layers through the substitution of Ca for \(Y\), the Néel temperature decreases rapidly with increasing \(x\) and superconductivity appears in the region of \(x \gtrsim 0.15\). The \(T_C\) reaches a maximum value of about 80 K at \(x = 0.5\).

In this paper, we first determine which of the Cu(1) and Cu(2) sites 3d M atoms occupy for \(\text{Pb}_x\text{Sr}_y\text{Y}\(_{1-x-y}\text{Ca}_x\text{(Cu}\(_{1-M}\)\(_{M}\))}_2\text{O}_8\) (M = Fe, Co, Ni, Zn, Ga), by means of high-resolution powder neutron diffraction and profile analysis. The samples of \(x = 0\) and \(y = 0.08\) were chosen for the measurements, because the single-phase samples were prepared easily in spite of the large \(y\) value. Next, we study effects of the Cu-site substitution on \(T_C\) for the high-\(T_C\) samples of \(x = 0.5\) in \(\text{Pb}_x\text{Sr}_y\text{Y}_{1-x-y}\text{Ca}_x\text{(Cu}\(_{1-M}\)\(_{M}\))\(_2\)O}_8\). We study the magnetism of these substituted samples from measurements of the magnetic susceptibility, too. Then, correlation between the site preference of M and the superconducting and magnetic properties is discussed.

**EXPERIMENTAL**

Ceramic samples of \(\text{Pb}_x\text{Sr}_y\text{Y}_{1-x-y}\text{Ca}_x\text{(Cu}\(_{1-M}\)\(_{M}\))\(_2\)O}_8\) were synthesized by a two-step solid-state reaction.

The powder neutron diffraction measurements were carried out at room temperature by means of the high-resolution powder neutron diffractometer HRPD at JRR-3M of JAERI. Radiation of monochromatized neutrons with the wavelength of 1.8232 Å was used in the experiment. The diffracted intensities were collected in the 2\(\theta\) angular range 15 - 155° in steps of 0.05°. The structural parameters were determined using the Rietveld profile refinement program Rietan\(^2\).

Resistivity measurements were made by a DC four-point probe method. The magnetic susceptibility was measured at 1 T with a SQUID magnetometer.

**RESULTS AND DISCUSSION**

Figure 1 shows typical powder neutron diffraction profiles for \(x = 0\) and \(y = 0.08\) in \(\text{Pb}_x\text{Sr}_y\text{Y}_{1-x-y}\text{Ca}_x\text{(Cu}\(_{1-M}\)\(_{M}\))\(_2\)O}_8\). Both observed intensities and calculated ones after the Rietveld profile refinement are represented. The Rietveld refinement is made on the basis of the structure model with the space group \(\text{Cmmm}\). The O(2) atoms in the PbO layer are split into two sub-sites equally, assigning the 8n site \((0,y,z)\). The sum of the occupation factors \(g\)'s of Cu(1) and M(1) in the Cu(1) site is constrained to be full, and that of Cu(2) and M(2) in the Cu(2) site is also constrained to be full. Moreover, the sum of \(g\) of M(1) and twice \(g\) of M(2) is constrained to be 0.08 \(x\) 3, because one Cu(1) site and two Cu(2) sites exist in the unit cell. The thermal parameters \(B\)'s of M(1) and M(2) are constrained to be the same as those of Cu(1) and Cu(2), respectively. Good agreements between the observed intensities and calculated ones after the Rietveld refinement are obtained. The refined structural parameters are listed in Table I. The \(B\) value of O(2) is large, indicating disordering of the O(2) atoms as pointed out in the literature\(^{11,12}\). Some unreasonable negative signs of \(g\) and \(B\) in Table I may be ignored. We wish to focus our attention only to the difference in \(g\) between M(1) and M(2). It is found that \(g\) of M(1) is larger than that of M(2) only for M = Fe and that it is reversed for M = Co, Ni, Zn and Ga. Therefore, it is conceivable that Fe atoms prefer the Cu(1) site to
the Cu(2) site, while Co, Ni, Zn and Ga atoms prefer the Cu(2) site to the Cu(1) site. However, detailed discussions on the distribution of M atoms in the Cu(1) and Cu(2) sites are avoided because of relatively wide error ranges in the g values. The B values of Cu(1) and M(1) for M = Fe are larger than those for any other M, which suggests that Fe atoms occupy the

Fig. 1. Typical powder neutron diffraction profiles for x = 0 and y = 0.08 in Pb$_2$Sr$_2$Y$_{(Cu_{1-x}M_x)}$O$_8$. (a) M = Fe. (b) M = Co. Observed intensities are represented by the points. Calculated ones after the Rietveld profile refinement are represented by the continuous line. The difference between the observed and calculated intensities is shown in the lower portion.

Cu(1) site leading to disordering in the Cu(1) site. In conclusion, it may be indicated in a broad way that Fe atoms occupy the Cu(1) site and that Co, Ni, Zn and Ga atoms occupy the Cu(2) site. Similar works with the powder neutron diffraction have been reported only for $M = Ni$). Their results are in agreement with ours that Ni atoms occupy the Cu(2) site.

As for $YBa_2Cu_{1-x}M_xO_3$ where also has two kinds of Cu sites in the unit cell, it has been shown that the trivalent ions such as Fe, Co and Ga prefer the Cu(1) site in the CuO chain, whereas, divalent ions of Ni and Zn prefer the Cu(2) site in the CuO$_2$ layer). These are partly different from our results on $PbSr_2YCu_{1-x}M_xO_3$. This may be ascribed to the difference in the oxygen-coordination of the Cu(1) site or in the valence of Cu(1) between the Y- and Pb-based systems.

Figure 2 displays the depression rate of $T_c$ through the Cu-site substitution for $x = 0.5$ in $Pb_{2}Sr_{1}Y_{1-x}Ca_{x}(Cu_{1-M}M_x)O_3$, where $T_c$ is defined at the midpoint of the superconducting transition curve in the $T$ vs $T$ plot. It is found that the depression of $T_c$ is most remarkable for $M = Ga$ and least for $M = Fe$. Compared with the data for $La_{2}Ba_{2}Cu_{1-M}M_xO_4$ shown in fig. 2, the dependence of the depression rate on $M$ is roughly similar to each other, except for $M = Fe$. The difference for $M = Fe$ will be attributed to the fact that Fe atoms occupy the Cu(1) site in the Pb-based system whereas they occupy the only Cu site in the CuO$_2$ layer in the La-based system. This indicates that the partial substitution for Cu(1) shows a little effect on the superconductivity. This is also inferred in comparison with the data for $YBa_2Cu_{1-M}M_xO_3$, shown in fig. 2. It seems that superconducting electrons flow locally in the CuO$_2$ layer so that the superconductivity is not so affected by disordering beyond the CuO$_2$ layer.

Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi$ in a magnetic field of 1 T for $x = 0.5$ and $y = 0.04$ in $Pb_{2}Sr_{2}Y_{1-x}Ca_{x}(Cu_{1-M}M_x)O_3$. The sudden drop in $\chi$ at low temperatures are due to the superconducting transition. For the non-substituted sample, $\chi$ slightly increases with decreasing temperature in the high temperature region above 100 K. The increase in $\chi$ with decreasing temperature in the high temperature region becomes marked through the partial Cu-site

---

Fig. 2. Depression rate of $T_c$ through the Cu-site substitution, $dT_c/dy$, for $x = 0.5$ in $Pb_{2}Sr_{1}Y_{1-x}Ca_{x}(Cu_{1-M}M_x)O_3$ (•). Data for $YBa_2Cu_{1-x}M_xO_3$ (•) and $La_{2}Ba_{2}Cu_{1-M}M_xO_4$ (△) are also plotted for comparison.

Fig. 3. Temperature dependence of the magnetic susceptibility $\chi$ in a magnetic field of 1 T for $x = 0.5$ and $y = 0.04$ in $Pb_{2}Sr_{2}Y_{1-x}Ca_{x}(Cu_{1-M}M_x)O_3$. 

---

244
substitution by every M. In every substituted sample, the temperature dependence of $\chi$ in the high-temperature region above 100 K is approximately expressed as a sum of a Curie term $C/(T-\theta)$ and a constant term $C_0$ independent of temperature, where $C$ and $\theta$ are the Curie constant and the Weiss temperature, respectively. As the Curie term increases with increasing $y$, magnetic moments are considered to be induced by not only magnetic Fe, Co and Ni ions but also nonmagnetic Zn and Ga ions. Assuming that the magnetic moments reside on the substituted M ions, the effective number of Bohr magnetons $p_{\text{eff}}$ per M ion is estimated from the value of $C$ with the equation, $C = N_p \mu_B^2 p_{\text{eff}}/(3k_B)$. Here, $N_p$, $\mu_B$, and $k_B$ are the number of M ions, the Bohr magneton and the Boltzmann constant, respectively. The values of $p_{\text{eff}}$ are listed in Table II for $x = 0.5$ and $y = 0.02$ and 0.04 in Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_{2-x}$M$_x$O$_{x+y}$. It is found that the values of $p_{\text{eff}}$ are almost independent of $x$ in the region of $y \leq 0.04$ and that they are large for M = Fe and Co, small for M = Zn and Ga, and intermediate for M = Ni.

First, we discuss the experimental values of $p_{\text{eff}}$ listed in Table II. As the Curie term increases with increasing $y$, it may be regarded as being due to localized spins of the substituted M ions. However, the case is not so simple, because the Curie term appears also through the substitution of nonmagnetic ions such as Zn$^{2+}$ and Ga$^{3+}$. The appearance of the Curie term for M = Zn and Ga may be understood from the following speculations $^3$ and $^4$. Although the long-range antiferromagnetic ordering of Cu$^{2+}$ spins in the CuO$_2$ layer for $x = 0$ in Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_{2-x}$O$_{x+y}$ is destroyed with increasing $x$, it is considered that there remains the short-range correlation between Cu$^{2+}$ spins also for the high-T$_c$ samples of $x = 0.5$. Accordingly, Cu$^{2+}$ spins in the CuO$_2$ layer are antiferromagnetically coupled within the short range as simply shown with a pair model in fig. 4(a), and so the Curie term due to free localized-moments does not appear in the $\chi$ vs T plot for the high-T$_c$ samples of $x = 0.5$ and $y = 0$. When nonmagnetic ions are partially substituted for Cu$^{2+}$ spins in the CuO$_2$ layer, unpaired Cu$^{2+}$ spins appear as shown in fig. 4(b), leading to the appearance of the Curie term. That is

| Table II. Experimental and calculated values of the effective number of Bohr magnetons $p_{\text{eff}}$ per M ion for $x = 0.5$ in Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_{2-x}$O$_{x+y}$. Two kinds of calculated values are listed. One is based on the 'free ion model,' and $p_{\text{eff}}$ values are given by $p_{\text{eff}} = 2S(S+1)$ with the spin quantum number $S$, depending on the spin state of the M ion. The other is calculated with the correction due to the antiferromagnetic correlation between Cu$^{2+}$ spins in the CuO$_2$ layer, and the $p_{\text{eff}}$ values are given by $p_{\text{eff}} = 2S(S+1)$ with the effective spin quantum number $S = |S - 0.21|$, depending on the spin state. The S values in the former and the $S^+$ values in the latter are described in the brackets. |
| --- |
| **Fe** | **Co** | **Ni** | **Zn** | **Ga** |
| $y = 0.02$ | $3.78$ | $3.46$ | $2.22$ | $1.01$ | $1.35$ |
| $y = 0.04$ | $3.85$ | $3.59$ | $2.20$ | $1.01$ | $1.02$ |
| **Fe$^{2+}$** | **Fe$^{3+}$** | **Co$^{3+}$** | **Ga$^{3+}$** | **Ni$^{2+}$** | **Zn$^{3+}$** | **Ga$^{3+}$** |
| high spin | $5.92 (5/2)$ | $4.90 (2)$ | $4.90 (2)$ | $3.97 (3/2)$ | $2.82 (1)$ | $1.00 (1)$ |
| intermediate spin | $3.87 (3/2)$ | $2.83 (1)$ | $2.83 (1)$ | $1.00 (1)$ | $1.00 (1)$ | $1.00 (1)$ |
| low spin | $1.72 (1/2)$ | $0$ | $0$ | $0$ | $0$ | $0$ |
| **calculation** |
| high spin | $5.49 (2.29)$ | $4.47 (1.79)$ | $4.47 (1.79)$ | $3.44 (1.29)$ | $2.38 (0.79)$ | $1.00 (0.21)$ |
| intermediate spin | $3.44 (1.29)$ | $2.38 (0.79)$ | $2.38 (0.79)$ | $1.00 (0.21)$ | $1.00 (0.21)$ | $1.00 (0.21)$ |
| low spin | $1.22 (0.29)$ | $1.01 (0.21)$ | $1.01 (0.21)$ | $1.22 (0.29)$ | $1.00 (0.21)$ | $1.00 (0.21)$ |

— 245 —
to say, the Curie terms for \( M = \text{Zn and Ga} \) are regarded as being due to the recovery of the free localized-spins of \( \text{Cu}^{2+} \). The experimental values of \( p_{\text{eff}} \) for \( M = \text{Zn and Ga} \) are almost equal to each other and are about 1.0. These values are smaller than the value, 1.73, calculated with \( S = 1/2 \) of \( \text{Cu}^{2+} \) and the equation \( p_{\text{eff}} = 2/S(S+1) \). The difference may result from the possible reduction of \( S \) due to the hybridization between the 3d,2 of the \( \text{Cu}(2) \) and 2p,0 of the \( 0(3) \) in the \( \text{CuO}_2 \) layer. The effective spin quantum number of \( \text{Cu}^{2+} \) in the \( \text{CuO}_2 \) layer, \( S_{\text{Cu}^{2+}} \), is estimated as 0.21 from the experimental values of \( p_{\text{eff}} \) for \( M = \text{Zn and Ga} \). These speculations are correct, the following is expected when magnetic ions are substituted for the \( \text{Cu}^{2+} \) spins in the \( \text{CuO}_2 \) layer. That is to say, the localized spin of the substituted magnetic ion is antiferromagnetically paired with the nearest \( \text{Cu}^{2+} \) spin with \( S_{\text{Cu}^{2+}} = 0.21 \) as shown in fig. 4(c). Consequently, the reduced Curie term is expected to be observed. The \( p_{\text{eff}} \) values per \( M \) ion, calculated with the equation \( p_{\text{eff}} = 2/S(S+1) \), are listed in Table II, depending on the spin state. On the other hand, when the \( \text{Cu}(1) \) site is partially replaced by \( M \) ions, the Curie term due to free localized-spins with \( S \) of the \( M \) ions is expected to be observed, for \( \text{Cu}(1) \) is nonmagnetic. The \( p_{\text{eff}} \) values per \( M \) ion calculated with the equation \( p_{\text{eff}} = 2/S(S+1) \) are also listed in Table II, depending on the spin state. Compared with the calculated values of \( p_{\text{eff}} \), the experimental ones of \( p_{\text{eff}} \) for \( M = \text{Co and Ni} \) approximately agree with the respective calculated-ones with the correction due to the antiferromagnetic correlation between \( \text{Cu}^{2+} \) spins in the \( \text{CuO}_2 \) layer. Consequently, it is indicated that Co atoms occupy the \( \text{Cu}(2) \) site as \( \text{Co}^{2+} \) in the high spin state and that Ni atoms also occupy the \( \text{Cu}(2) \) site as \( \text{Ni}^{2+} \) in the high spin state. On the other hand, the experimental value of \( p_{\text{eff}} \) for \( M = \text{Fe} \) is in agreement with the calculated one without the correction. Consequently, it is indicated that Fe atoms occupy the \( \text{Cu}(1) \) site as \( \text{Fe}^{3+} \) in the intermediate spin state. The intermediate spin state of \( \text{Fe}^{3+} \) is understood as being due to the crystal-field effect. That is, the \( \text{Cu}(1) \) site is surrounded on the upper and lower sides by two \( 0(2) \) atoms so that the crystal field, which \( \text{Cu}(1) \) feels, is uniaxial. When the uniaxial anisotropy is very strong and the energy difference between the 3d,2 level and the other 3d-ones is larger than the atomic-exchange energy, five 3d-electrons of \( \text{Fe}^{3+} \) occupy the lower four levels according to the Hund's rule. Consequently, \( \text{Fe}^{3+} \) is considered to take the intermediate spin state. In contrast, the high spin state of \( \text{Co}^{2+} \) and \( \text{Ni}^{2+} \) is understood as follows. The \( \text{Cu}(2) \) site is surrounded by
five O atoms like a pyramid so that the crystal field, which Cu(2) feels, is more isotropic than what Cu(1) feels. Therefore, the energy difference among 3d-electron states in the Cu(2) site due to the crystal field is smaller than the atomic-exchange energy, and Co$^{2+}$ and Ni$^{2+}$ take the high spin state according to the Hund's rule.

Thus the sites of M atoms estimated from the above speculations are in good agreement with those estimated from the neutron diffraction as mentioned in 3.1. Moreover, the experimental values of p_{eff} and spin states of the substituted M ions are fairly well explained from the speculations. These suggest that the speculations are not so irrelevant. Furthermore, our results may provide an experimental proof that there remains antiferromagnetic correlation between Cu$^{2+}$ spins in the Cu(2) site in the normal state even for the high-T_c samples of x = 0.5. It attracts great interests whether the antiferromagnetic correlation is indispensable to the appearance of high-T_c superconductivity or not. In addition, it may be said that the appearance of the Curie term through the partial substitution of Zn and Ga is a proof that Zn and Ga atoms occupy the Cu(2) site, as confirmed from the neutron diffraction.

As for the mechanism of the suppression of superconductivity through the partial substitution of Co, Ni, Zn and Ga for Cu(2), no clear correlation between p_{eff} and the depression rate of T_c has been found. Accordingly, the suppression of superconductivity can not be simply ascribed to the pair-breaking mechanism due to localized spins. What correlates most with the depression rate of T_c may be the difference in the 3d-electron numbers between M and Cu. At present, however, this leads to only the common conclusion that the 3d-electron state of Cu is very important to the high-T_c superconductivity. The detailed mechanism of the suppression of superconductivity is an open question.

REFERENCES

CRYSTAL STRUCTURES OF NEW CUPRATES CONTAINING CO$_3$ ANALYZED BY THE RIETVELD METHOD OF NEUTRON POWDER DIFFRACTION

Y. Miyazaki, H. Yamane, T. Kajitani, K. Hiraga, Y. Morii, S. Funahashi and T. Hirai

Institute for Materials Research
Tohoku University
Katahira 2-1-1, Sendai-shi, Miyagi-ken, 980 Japan

Department of Physics
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

New compounds containing CO$_3$ groups, Sr$_2$CuO$_2$(CO$_3$), (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$ and (C$_{0.35}$Cu$_{0.65}$)Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)$_2$Cu$_2$O$_7$, were prepared as stable phases at 1273-1303 K in a flowing gas of O$_2$-CO$_2$. The crystal structures of these compounds were refined by means of the Rietveld analysis for neutron powder diffraction data collected using a high resolution powder diffractometer (HRPD) in the JRR-3M reactor hall of the Japan Atomic Energy Research Institute (JAERI). Positions of CO$_3$ groups were satisfactorily determined. The distances of C-O bonds in the CO$_3$ groups were around 1.3 Å and the O-C-O angles were almost equal to the ideal bond angle of 120°.

INTRODUCTION

In the last several years, a number of new high-$T_c$ cuprate superconductors have been discovered$^{1-3}$. The authors succeeded in preparing a single phase of Sr$_2$CuO$_2$(CO$_3$) in an atmosphere of O$_2$-CO$_2$$^{4}$. Subsequently, we discovered new compounds containing CO$_3$ groups, (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$ and (C$_{0.35}$Cu$_{0.65}$)Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)$_2$Cu$_2$O$_7$.$^{5,6}$ These three compounds have become new superconductors by substitution of some part of the elements with other elements and by high pressure oxygen annealing$^{6,8}$.

The Rietveld method of neutron powder diffraction has been demonstrated to be a highly powerful tool for determination of the oxygen positions and contents in superconducting cuprates and related compounds. We applied this method for crystal structure analysis of the newly discovered cuprates containing CO$_3$ groups. The positions of CO$_3$ groups, which could not be determined by X-ray diffraction, were determined from neutron diffraction data measured with a high resolution powder diffractometer (HRPD) at the Japan Atomic Energy Research Institute (JAERI). The present paper describes the crystal structure of the cuprates containing CO$_3$ groups analyzed by neutron powder diffraction.
EXPERIMENTAL

Sr$_2$CuO$_2$(CO$_3$), (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$ and (C$_{0.35}$Cu$_{0.65}$)Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)Cu$_2$O$_9$ were prepared from SrCO$_3$, Y$_2$O$_3$, CeO$_2$ and CuO powders. These powders were mixed in an agate mortar and pressed into pellets. The pellets were heated to 1273-1303 K in a flowing gas of O$_2$-CO$_2$. The CO$_2$ partial pressures were 0.01-0.02 MPa$^{4-6}$. Neutron powder diffraction data were collected from 2θ = 23.0° to 150.0° using HRPD at JAERI. The incident beam was monochromatized to λ = 1.8232 Å with the (331) plane of focused Ge single crystals.

Rietveld analysis of neutron powder diffraction patterns was carried out using the program, "RIETAN"$^{9}$. Interatomic distances and angles, together with estimated standard deviations, were computed using a program, "ORFFE"$^{10}$.

RESULTS AND DISCUSSION

1. Sr$_2$CuO$_2$(CO$_3$)

Figure 1 illustrates the obtained neutron powder diffraction intensity distribution of Sr$_2$CuO$_2$(CO$_3$), a fitted pattern and the differences between the observations and calculations. The tick marks represent the positions of possible Bragg reflections. The differences between the observed and the calculated intensities indicate sufficient agreement. The final R-factors, adopting the space group $I4$ determined from electron diffraction, were $R_W$ = 11.01, $R_P$ = 8.34, $R_C$ = 3.93, $R_I$ = 5.05 and $R_F$ = 3.52%. The lattice parameters were refined to be $a$ = 7.8052(1) and $c$ = 14.9941(3) Å.

Figure 2 shows the crystal structure of Sr$_2$CuO$_2$(CO$_3$). This structure is composed of an alternative stacking of a [CuO$_2$] plane and a [Sr$_2$CO$_3$] layer. In the CO$_3$ group, the C atom is coordinated by the triangular planar O atoms. Each triangular CO$_3$ group is orderly located perpendicular to the neighboring CO$_3$ groups along the $a$-axis. The basic crystal structure of an

![Graph](image-url)

**Fig. 1.** Rietveld refinement profile and neutron powder diffraction data for Sr$_2$CuO$_2$(CO$_3$).
averaged lattice, where the CO₃ groups were presumed to orient statistically, was reported by Babu et al.\textsuperscript{11} assuming the space group \textit{P4/mmm} and the lattice parameters of \(a = 3.9033(2)\) and \(c = 7.4925(4)\) Å. The sample they used contained small amount of SrCO₃ as a second phase.

Recently, a new superconductor, (Sr\(_{1-x}\)Ba\(_x\))\(_2\)Cu\(_{1+y}\)O\(_{2+2y+6}\)(CO\(_3\))\(_{1-y}\) with an onset transition temperature \((T_c)\) up to \(\sim 40\) K, was synthesized under high pressure of oxygen \((P_{O_2} = 5.0\) MPa\)\textsuperscript{7}). In the structure of this superconductor, about half of the Sr atoms are replaced by Ba atoms and 10% of the CO₃ groups are replaced by CuO\(_x\)\textsuperscript{12}.

2. \((C_{0.4}Cu_{0.6})Sr_2(Y_{0.86}Sr_{0.14})Cu_2O_7\)

Diffuse superlattice reflections having a period of \(a^*/2\) to \(a^*/3\) and \(c^*/2\) were observed in the electron diffraction patterns of \(a^*\)-\(c^*\) and \(a^*-b^*\) planes of \((C_{0.4}Cu_{0.6})Sr_2(Y_{0.86}Sr_{0.14})Cu_2O_7\)\textsuperscript{5}). The basic structure of this compound was determined from the neutron powder diffraction data, disregarding very weak superlattice diffractions. Probable space groups for the basic structure are \textit{Pmmm}, \textit{P222} and \textit{Pmm2}, because no systematic absence of fundamental spots was observed. The space group \textit{Pmnm} was adopted for structure analysis. The final \(R\)-factors were \(R_{wp} = 11.53\), \(R_p = 9.14\), \(R_e = 4.82\), \(R_1 = 5.78\) and \(R_F = 3.70\%\) and the refined lattice parameters were \(a = 3.8306(2)\), \(b = 3.8512(1)\) and \(c = 11.1881(5)\) Å. Figure 3 (a) shows the positions of the refined atomic sites in the basic structure projected on (010). A proposed local structure on the basis of the basic structure and

---

\textbf{Fig. 2.} Crystal structure of \(Sr_2CuO_2(CO_3)\).

\textbf{Fig. 3.} Projection of the refined site positions (a), and local crystal structure of \((C_{0.4}Cu_{0.6})Sr_2(Y_{0.86}Sr_{0.14})Cu_2O_7\) (b).
high resolution electron microscopic images\textsuperscript{5,13} is represented in Fig. 3 (b).

The structure of this new compound is closely related to \( \text{YBa}_2\text{Cu}_3\text{O}_{7-y} \). Forty percent of the \( \text{CuO}_3 \) chains in the \( \text{YBa}_2\text{Cu}_3\text{O}_{7-y} \) structure are substituted with \( \text{CO}_3 \) groups. The unit of the basic structure is composed of a \( [\text{Sr}_2(\text{C,Cu})\text{O}_3] \) layer, a \([\text{Y,Sr}]\) layer and two \([\text{CuO}_2]\) planes. The triangular plane of the \( \text{CO}_3 \) groups lies in the \( a-c \) plane, and the \( \text{CuO}_3 \) chains are located along the \( b \)-axis.

A new superconductor, \((\text{Y}_{1-x}\text{Ca}_x)_{0.95}\text{Sr}_{2.05}\text{Cu}_{2.4}\text{O}_y(\text{CO}_3)_{0.6}\), \( T_c(\text{onset}) = 66 \text{ K} \), was synthesized by substitution of elements in the \([\text{Y,Sr}]\) layer with \text{Ca} atoms and annealing at high pressure oxygen of \( P\text{O}_2 = 10 \text{ MPa} \) at 973 K\textsuperscript{8}.

3. \((\text{C}_{0.35}\text{Cu}_{0.65})\text{Sr}_2(\text{Y}_{0.73}\text{Ce}_{0.27})_2\text{Cu}_2\text{O}_9\)

The basic structure of \((\text{C}_{0.35}\text{Cu}_{0.65})\text{Sr}_2(\text{Y}_{0.73}\text{Ce}_{0.27})_2\text{Cu}_2\text{O}_9\) was determined because superlattice reflections derived from ordered \( \text{CO}_3 \) arrangement were very weak in the neutron powder pattern. The final \( R \)-factors assuming the space group \textit{Imma} were \( R_{wp} = 10.19, R_p = 7.88, R_e = 5.70, R_I = 5.98 \) and \( R_F = 5.22\% \). The refined lattice parameters were \( a = 3.8355(4), b = 3.8347(4) \) and \( c = 27.6918(6) \text{ Å} \). Figure 4 (a) shows a schematic view of the atomic site positions of the basic structural analysis projected on \((010)\). A proposed local structure is

\[
\begin{array}{c}
\text{(a)} \\
\text{(b)}
\end{array}
\]

\textbf{Fig. 4.} Projection of the refined site positions (a), and local crystal structure of \((\text{C}_{0.35}\text{Cu}_{0.65})\text{Sr}_2(\text{Y}_{0.73}\text{Ce}_{0.27})_2\text{Cu}_2\text{O}_9\) (b).
illustrated in Fig. 4 (b).

This structure can be represented with the layered structure of [CuO$_2$] planes, [Sr$_2$(CuO)$_3$] layers and fluorite-type [CeO$_2$] layers. The ratio of C and Cu atoms in the [Sr$_2$(CuO)$_3$] layer is 0.35:0.65. The triangular CO$_3$ groups lies in the a - c plane and the CuO$_3$ chains are located along the b - axis, as in the structure of (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$. The compound annealed at 1023 K under a high oxygen pressure of 90 MPa became a superconductor with $T_c = 18$ K$^6$.

4. The C-O bond distances and O-C-O angles of the CO$_3$ groups

Table 1 shows determined C-O bond distances and O-C-O angles of the CO$_3$ groups in Sr$_2$CuO$_2$(CO$_3$)$_2$, (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$ and (C$_{0.35}$Cu$_{0.65}$)Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)Cu$_2$O$_9$. The C-O distances and O-C-O angles reported for some compounds, CaCO$_3$(calcite)$^{14}$, Nd$_2$O$_2$(CO$_3$)$_2$$^{15}$ and Na$_2$Cu(CO$_3$)$_2$$^{16}$ are also summarized in Table 1.

In the calcite, the C atom is situated at the center of the three planar O atoms. The distance between the C atom and each O atom is 1.294 Å and the angle of O-C-O is 120°. The CO$_3$ groups in the oxycarbonates of Nd$_2$O$_2$CO$_3$ and Na$_2$Cu(CO$_3$)$_2$ have nearly triangular planar coordinations. The C-O distances reported for these compounds range from 1.22 to 1.45 Å, and the angles of O-C-O slightly deviate from the ideal value of 120°.

The distances of C-O in the CO$_3$ groups of Sr$_2$CuO$_2$(CO$_3$)$_2$ are 1.248-1.303 Å, which lie well within the range of values observed for the related compounds mentioned above. The O-C-O angles of the CO$_3$ group are around 120° and their sum is 360°, which indicates that the triangular coordinated C atom and the three O atoms are in a plane. In the (C$_{0.4}$Cu$_{0.6}$)Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$ and (C$_{0.35}$Cu$_{0.65}$)Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)Cu$_2$O$_9$ structures, the C-O distances are 1.25-1.33 Å, the O-C-O angles are 118.4-120.8° and their sum is 360°. The C atoms in these compounds are also coordinated by the three planar O atoms.

Table 1  Comparison of the C-O distances (Å) and O-C-O angles (°) in carbonates and oxycarbonates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-O distance (Å)</th>
<th>O-C-O angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$CuO$_2$(CO$_3$)$_2$</td>
<td>1.248(39), 1.263(41), 1.303(29)</td>
<td>111.3(45), 122.0(44), 126.7(26)</td>
</tr>
<tr>
<td>(C$<em>{0.4}$Cu$</em>{0.6}$)Sr$<em>2$(Y$</em>{0.86}$Sr$_{0.14}$)Cu$_2$O$_7$</td>
<td>1.31(22), 1.30(8)</td>
<td>118.4(70), 120.8(35)</td>
</tr>
<tr>
<td>(C$<em>{0.35}$Cu$</em>{0.65}$)Sr$<em>2$(Y$</em>{0.73}$Ce$_{0.27}$)Cu$_2$O$_9$</td>
<td>1.25(29), 1.33(10)</td>
<td>119.8(77), 120.1(38)</td>
</tr>
<tr>
<td>CaCO$_3$ (Calcite)$^{14}$</td>
<td>1.294(4)</td>
<td>120.0</td>
</tr>
<tr>
<td>Nd$_2$O$_2$(CO$_3$)$_2$$^{15}$</td>
<td>1.02(22), 1.45(10)</td>
<td>103.9, 128.6</td>
</tr>
<tr>
<td>Na$_2$Cu(CO$_3$)$_2$$^{16}$</td>
<td>1.22(2), 1.29(2), 1.36(2)</td>
<td>117.5(16), 118.7(16), 123.8(16)</td>
</tr>
</tbody>
</table>
CONCLUSION

The crystal structures of the new compounds containing CO$_3$ groups, Sr$_2$CuO$_2$(CO$_3$), (Cu$_{0.4}$Cu$_{0.6}$)$_2$Sr$_2$(Y$_{0.86}$Sr$_{0.14}$)$_2$Cu$_2$O$_7$ and (Cu$_{0.35}$Cu$_{0.65}$)$_2$Sr$_2$(Y$_{0.73}$Ce$_{0.27}$)$_2$Cu$_2$O$_9$, were refined from neutron powder diffraction data by means of the Rietveld method. Precise positions of CO$_3$ groups were satisfactorily determined. The newly discovered superconductors containing CO$_3$ groups are derived from these compounds. The knowledge of the crystal structures of these compounds may be useful in finding other new superconductors containing CO$_3$ groups.

ACKNOWLEDGMENTS

This work was supported, in part, by a Grant-in-Aid for Scientific Research on Priority Areas, "Science of High-$T_c$ Superconductivity" and a Grant-in-Aid for New Programs under Contract No. 03NP0501 given by the Ministry of Education, Science and Culture, Japan.

REFERENCES

P-110

POLARIZATION ANALYSIS ON TWO-DIMENSIONAL ANTIFERROMAGNET ErFe$_2$O$_{4.5}$

Hijiri KITO, Jun AKIMITSU, *Kiiiti SIRATORI, and **Masakazu NISHI

Department of Physics, Aoyama-Gakuin University, Setagaya-ku, Tokyo, 157

*Department of Physics, Osaka University, Toyonaka, Osaka 560

**The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, 106

ABSTRACT

In order to separate the nuclear and magnetic components of the quasi two-dimensional short range order in the non-stoichiometric ErFe$_2$O$_{4.5}$, the polarization analysis on the single crystal was performed. Our main experimental results are:

1) we observed the broad nuclear Bragg peaks (1/3, 1/3, 1/3, 6), (1/3, 1/3, 1/3, 12), (2/3, 2/3, 4) and (2/3, 2/3, 13) at room temperature.

2) magnetic Bragg lines were observed at 150K, accompanying the developing broad nuclear Bragg peaks.

3) a modulated structure on the magnetic Bragg line was observed at 10K, indicating that the two-dimensional Bragg line gradually develops to the three-dimensional Bragg point. This modulated structure can be interpreted as the magnetic interaction between adjacent Fe$_2$O$_3$ layers (W-layers).

INTRODUCTION

ErFe$_2$O$_{4.5}$ is one of the rare earth iron oxide compounds RFe$_2$O$_{4.5}$ (R: Y, Ho, Er, Tm, Yb and Lu) family with the space group P3m 1). The crystal structure is shown in Figure 1. It has a hexagonal layered structure composed of the RO unit (U-layer) and Fe$_2$O$_3$ unit (W-layer) stacked alternately along the c-axis. The two adjacent W-layers are separated each other, being expected the marked magnetic two-dimensionality and to be a two-dimensional triangular Ising antiferromagnet at low temperature. Neutron diffraction at low temperatures demonstrated Bragg lines along the c* axis below the Néel temperature, instead of Bragg spots for the ordinary three-dimensional magnetic structure 2).

Fe$^{3+}$ and Fe$^{2+}$ ions occupy the same crystallographic site in W-layer, suggesting that electrons hop among Fe ions and resulting in rather high electrical conduction at room temperature. The non-stoichiometric YFe$_2$O$_{4}$-δ has two magnetic characteristics: the appearance of the parasitic ferrimagnetism and two-dimensional spin ordering. On the other hand, the nearly stoichiometric YFe$_2$O$_4$ shows the different magnetic and crystallographic behavior: two-step first order phase transition appears and three-dimensional magnetic
Figure I. 
Crystal structure of RFe$_2$O$_4$ and four interlayer magnetic interaction parameters $q$, $s$, $t$ and $u$. 

Order develops$^3)$. In LuFe$_2$O$_4$, even in the stoichiometric specimen, the three-dimensional magnetic phase transition does not take place and parasitic ferrimagnetism appears at low temperature. An nearly stoichiometric ErFe$_2$O$_4$ is a crucial material locating between two different physical characteristics: one-step first order phase transition appears and three-dimensional magnetic order develops$^4)$, on the other hand, a physical properties of the nonstoichiometric ErFe$_2$O$_{4.8}$ is similar to that of the stoichiometric LuFe$_2$O$_4$. These characteristics may be originated from the oxygen vacancy $\delta$ and R ion size. Ion sizes of $\text{VIY}^{3+}$, $\text{VI}_{\text{Er}}^{3+}$ and $\text{VI}_{\text{Lu}}^{3+}$ ion sizes are $r_e(\text{VIY}^{3+}) = 0.90 \ \text{Å}$, $r_e(\text{VI}_{\text{Er}}^{3+}) = 0.89 \ \text{Å}$, and $r_e(\text{VI}_{\text{Lu}}^{3+}) = 0.86 \ \text{Å}$, where $r_e$ and the roman numeral represent the effective ionic radius$^5)$, and coordination number, respectively.

The process of how to develop the three-dimensional magnetic order from the two-dimensional magnetic order are complicated. The spin and the charge ordering are related each other$^6)$. The charge-spin structure model was recently proposed by K. Siratori, et al.$^7)$.

In this note, we discuss the interlayer magnetic interactions of the three-dimensional spin ordering along the $c$-axis through the polarized neutron diffraction data in the nonstoichiometric ErFe$_2$O$_{4.8}$.

**EXPERIMENTAL AND RESULTS**

A single crystal was grown by the floating zone melting method under the controlled O$_2$ partial pressure Po$_2$ using CO$_2$-CO gas mixture. The oxygen vacancy was determined to be $\delta = 0.06(1)$ by the thermogravimetric method.

The experiments were carried out by the double-axis spectrometer, T1-1, used for the elastic scattering of the neutrons with a wavelength of 2.408 Å and polarized neutron diffraction experiments were carried out by the triple-axis spectrometer, PONTA, used for
Figure II. Temperature dependences of observed (1/3 1/3 l):
(A) room temperature,
(B) 150K,
(C) 41K and
(D) 11K.
the elastic scattering of the polarized neutrons with a wavelength of 1.412 Å, installed at the JRR-3M reactor at J.A.E.R.I., Tokai. Diffraction intensities were examined for the magnetic Bragg lines at around \((\frac{n}{3}, \frac{n}{3}, l)\) \((n = 1, 2)\) at various temperatures. Observed data for \((\frac{1}{3}, \frac{1}{3}, l)\) line taken at \(T = 150K\) are shown in Figure II.

The nuclear diffuse peaks \((\frac{1}{3}, \frac{1}{3}, -6), (\frac{1}{3}, \frac{1}{3}, -12)\) were observed at room temperature. The magnetic Bragg line was observed at 150K accompanying the developing nuclear diffuse peaks. The two-dimensional magnetic line has a modulated structure at 10K. This indicates that the two-dimensional Bragg line grows up to three-dimensional Bragg point.

The magnetic part \((d\sigma / d\Omega)_M\) and the nuclear part \((d\sigma / d\Omega)_N\) can be separated by using the polarized neutron technique. The magnetic part \((d\sigma / d\Omega)_M\) was given as

\[
(d\sigma / d\Omega)_M = f_M^2 \times L(Q) \times S_{\perp}(Q) \times |F_M|^{2}
\]

Here, \(f_M\) is a magnetic form factor of Fe ions, \(F_M\) is a structure factor, \(L(Q)\) is a Lorentz factor and \(S_{\perp}(Q)\) is the perpendicular component of Fe spins for \(Q\) vector.

Figure III (A) and (B) show the obtained nuclear and magnetic structure factor of the \((\frac{1}{3}, \frac{1}{3}, l)\) and \((\frac{2}{3}, \frac{2}{3}, l)\) line at 10K. The temperature dependences of \((\frac{1}{3}, \frac{1}{3}, 0)\) and \((\frac{2}{3}, \frac{2}{3}, 0)\) are also shown in Figure IV.

Although the nuclear parts for \(\frac{1}{3}, \frac{1}{3}, 0\) and \(\frac{2}{3}, \frac{2}{3}, 0\) were almost temperature independent, magnetic part was observed about 250K and they decreased below 40K.

Here, four parameters \(q, s, u\) and \(t\) are introduced, which represent the strength of the magnetic correlations between the inter- and inter-W layer unit (see Figure I). For example, if the two net spins in the W layer unit have the 2:1 (or 1:2) arrangement, \(s = +1\) (ferromagnetic case); if one net is 2:1 and the other net is 1:2, then \(s = -1\) (antiferromagnetic case). An intermediate value of \(s\) represents the probability of occurrence of the two cases. The situation is the same on the another parameters

The square of the structure factor \(|F_M|^2\) at \((\frac{1}{3}, \frac{1}{3}, l)\) line (or \((\frac{2}{3}, \frac{2}{3}, l)\) line) can be calculated as

\[
|F_M|^2 \propto 3 + 2u \cos \left(2\pi l (1/3 - z_0)\right)
\]  \hspace{5cm} (1)

where, \(z_0\) is the distance between two triangular nets of Fe atoms in the W layer unit. It is noticed that \(|F_M|^2\) depend only on the parameter \(u\).

The magnetic ordering was two-dimensional at 150K; Fe spin ordered randomly in a each
Figure III.
modified diffraction patterns
at 10K for
(A) \((1/3 \; 1/3 \; l)\) and
(B) \((2/3 \; 2/3 \; l)\).

![Graph A](image1)

![Graph B](image2)

Figure IV.
Temperature dependences
of the peak intensity for
modified \((1/3 \; 1/3 \; 0)\) and
\((2/3 \; 2/3 \; 0)\).

![Graph C](image3)
W layer unit because no modulated magnetic Bragg line were observed (i.e. the parameter \( u \) is \( \approx 0 \)), however, the modulated magnetic Bragg lines were observed at 11K, suggesting that the magnetic structure should be modulated by the weak antiferromagnetic correlation between two W layer units at 11K.

We tried to fit the theoretical curve (formula (1)) to the experimental data of \((1/3 \ 1/3 \ l)\) and \((2/3 \ 2/3 \ l)\) line (see Figure V). Although, small systematic errors between experimental and theoretical results can be seen, agreements are satisfactory. On the other hand, the appearance of the nuclear parts for \((1/3 \ 1/3 \ l)\) and \((2/3 \ 2/3 \ l)\) were complicated. Detailed analysis is now in progress.

Figure V.
experimentally obtained
magnetic structure factor
\( |F_M|^2\) for \((1/3 \ 1/3 \ l)\) and
\((2/3 \ 2/3 \ l)\).

Dotted and dot-dashed lines show the theoretical curve shown in the formula (1).

ACKNOWLEDGEMENTS

The authors would like to express their thanks to S.Takekawa for the support of growing the single crystal and to Dr. Y.Tsunoda for assisting the experiments.

REFERENCES


— 259 —
PHONON DISPERSION IN LAYERED STRUCTURE ErFe$_2$O$_{4-\delta}$

H. KITO, S. FUNAHASHI$^+$, K. SIRATORI$^{++}$ and J. AKIMITSU

Department of Physics, Aoyama - Gakuin University, Setagaya-ku, Tokyo 157
$^+$Department of Physics, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11
$^{++}$Department of Physics, Osaka University, Toyonaka, Osaka 560

ErFe$_2$O$_{4-\delta}$ has a hexagonal layered structure. Equal number of divalent and trivalent iron atoms are distributed randomly on the double triangular lattice at room temperature. This compound has two remarkable characteristics: One is the strong two-dimensional spin correlation in the hexagonal c-planes. This is due to the crystallographic reason that the two adjacent double iron oxide layers are largely separated each other. Another is the charge ordering of Fe$^{2+}$ and Fe$^{3+}$ resulting in the crystallographic distortion at low temperature. The correlation between charge and spin ordering which can be expected in this system, which suggest that phonon and magnon are affected each other.

We measured the phonon dispersion curve of ErFe$_2$O$_{4-\delta}$ using large single crystal. The single crystal was grown from T.S.F.Z. method. The experiment was performed by using a triple axis spectrometer [TAS-1] installed at JRR-3 reactor. The constant Q scans were carried out at [0+0.4 0+0.4 12], [0 0 12+3], [1+0.5 1+0.5 0] and [1 1 0+3] reciprocal points. Detailed analyses are now in progress.
CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF LnBa$_2$Cu$_4$O$_8$ (Ln = Ho, Er, Y, Dy and Gd) SUPERCONDUCTORS

+Toru. ISHIGAKI, +Kazuya. MORI, +Yasuhiro. KAWAGUCHI,
*Susumu. KATANO, *Satoru. FUNAHASHI and +Yoshikazu. HAMAGUCHI

+Department of Materials Science and Engineering,
Muroran Institute of Technology
Mizumoto-cho, Muroran-shi, Hokkaido, 050 Japan

*Department of Physics, JAERI
Tokai-mura, Naka-gun, Ibaraki, 319-11 Japan

ABSTRACT

Bulk Superconductors of LnBa$_2$Cu$_4$O$_8$ (Ln = Er, Ho, Y, Dy and Gd) which share the 124 structure of YBa$_2$Cu$_4$O$_8$ were synthesized by using hot isostatic pressing (HIP) treatment. The crystal structure at room temperature was refined from the neutron and X-ray powder diffraction data by Rietveld analysis. $T_c$ of our samples are showed monotonous decreasing from highest 84.1 K (Ln = Er) to 77.3 K (Ln = Gd) following the ionic radius. Madelung energy calculation from refined structural parameters show the hole concentration on CuO$_2$ plane. These result show that the substitution of lanthanoid elements to Y site of YBa$_2$Cu$_4$O$_8$ induce 'chemical pressure' effect.

INTRODUCTION

YBa$_2$Cu$_4$O$_8$ (124) is a superconductor with $T_c$ a little lower than 80K. It has a crystal structure (fig. 1) similar to that of YBa$_2$Cu$_3$O$_{7-δ}$ contains double chains of edge-sharing [CuO$_4$] square plane along $b$-axis of unit cell. YBa$_2$Cu$_4$O$_8$ shows a marked increase in $T_c$ with pressure (pressure effect); a linear rise of $T_c$ with $dT_c/dp = 5.5$ K GPa$^{-1}$ has been observed up to 2 GPa.

Morris et al. reported that the compounds in which lanthanoid elements (Er, Ho, Gd, Dy and Tm) were substituted for Y also showed superconductivity, but $T_c$ of these compounds were lower than that of YBa$_2$Cu$_4$O$_8$, although lattice parameters were increased according to ionic radius of lanthanoid elements. The substitution of smaller lanthanoid elements such as Er$^{3+}$ (ionic radius is 0.1004 nm$^4$) to Y$^{3+}$ ions (0.1019 nm) will cause decreasing of lattice parameters. This means
that 'chemical pressure' is applied to the crystal lattice and increasing of $T_c$ should be expected.

In this study, we prepared the single phase of LnBa$_2$Cu$_4$O$_8$ (LBCO) (Ln = Ho, Er, Y, Dy, Gd) using hot isostatic pressing (HIP) treatment to reconfirm about the relation between $T_c$ and substituted lanthanoid element. The crystal structure is refined by Rietveld analysis of X-ray and neutron powder diffraction data. The hole distribution between the CuO$_2$ plane and double chain has been determined from the Madelung-energy calculation based on the refined structural parameters. The result of the calculation gives a reasonable explanation for the increasing of $T_c$.

**EXPERIMENTAL**

The samples of LBCO were prepared by a hot isostatic pressing (HIP) technique. Ln$_2$O$_3$ (Ln = Ho, Er, Y, Dy and Gd), BeCO$_3$ and CuO powders were mixed in ethanol and calcined at 900 °C for 24 hours. The resulting powder was pressed into pellets, sintered at 900 °C and then post-annealed in a mixed gas (80%Ar + 20%O$_2$) at 170 MPa and 1070 °C for 5 hours using a furnace for hot isostatic pressing. The samples became almost single phase checked by X-ray powder diffraction.

The superconducting transition temperature was determined by electrical resistivity measurements.

Neutron powder diffraction experiments were carried out for three samples (Ln = Er, Y and Ho). The room temperature data was measured by using a high resolution powder diffractometer, HRPD, installed in JRR-3M of Japan Atomic Research Institute (JAERI). The neutron wave length were 0.1832 nm. The structural parameters were refined with Rietveld analysis program RIETAN. Because of the containment of a very mall amounts of CuO in samples, the neutron diffraction data were analyzed using the feature of multi-phase refinement in RIETAN by fixing the fractional coordinate of CuO at those described in the literature.7) A LBCO:CuO weight ratio was determined to be about 0.995:0.005 from the scale factors of the two compounds. The coherent scattering length, $b$, used for the refinement was 7.75 fm (Y), 8.03 fm (Er), 8.08 fm (Ho), 5.25 fm (Ba), 7.718 fm (Cu) and 5.803 fm (O).8) The initial structural
parameters model of LBCO was based on that of YBa$_2$Cu$_4$O$_8$ reported by Yamada et al. Its space group is Amm2 (No. 65) with Ln (= Y, Ho and Er) at 2c (1/2, 1/2, 0), Ba and O(2) at 4j (1/2, 0, z) and Cu(1), Cu(2), O(1), O(3) and O(4) at 4i (0, 0, z). All sites were regarded as being fully occupied, and the occupation factors were fixed at 1.0. Isotropic thermal parameters, B, were refined with all samples.

RESULTS

Figure 2 shows the temperature dependence of electrical resistivity of LBCO. The obtained $T_c$ is plotted against the ionic radius of rare earth elements in Fig. 3, and the data of Morris et al. also plotted for comparison. $T_c$ of our samples decreases monotonically from 84.1 K (Ln = Er) to 77.3 K (Ln = Gd) with the increase of ionic radius. $T_c$ of Morris et al. were lower than its YBa$_2$Cu$_4$O$_8$ and almost constant against the change of ionic radius. The X-ray pattern of DyBa$_2$Cu$_4$O$_8$ in ref. 3 seems to have impurity phase, which may make decreasing of $T_c$ in these samples.

The final structure parameters of LBCO (Ln = Er, Y and Ho) refined from neutron diffraction data were listed in Table 1. Table 2 gives the interatomic distances, l, calculated with ORFFE. Figure 4 illustrates the final result of observed, calculated and difference patterns for ErBa$_2$Cu$_4$O$_8$. The diffraction pattern includes 176 reflections for ErBa$_2$Cu$_4$O$_8$ and 49 for CuO reflections between 20.0° and 150.0° in a 2θ range.

![Graph](image_url)

**Fig. 2.** Temperature dependence of resistivity for LnBa$_2$Cu$_4$O$_8$ (Ln = Er, Ho, Y, Dy and Gd). Numbers on this figure represent the kind of lanthanoid elements: 1: Er, 2: Ho, 3: Y, 4: Dy and 5: Gd.
Fig. 3. The $T_c$ of LnBa$_2$Cu$_4$O$_8$ as a function of ionic radius of Lanthanoid elements. Closed circle indicate our result. Open square also represent the result of Morris et al.\textsuperscript{3)}

Fig. 4. Rietveld refinement pattern of ErBa$_2$Cu$_4$O$_8$. Plus symbols represent the raw diffraction data points which are overlapped by a continuous line, the calculated pattern. Two set of tick mark indicate positions of allowed bragg reflections for ErBa$_2$Cu$_4$O$_8$ (upper) and CuO (lower). $\Delta y_1$ at the bottom is difference between the observed and calculated intensities in the same scale.
Table I
Final result of the Rietveld refinement for LBCO at RT. As described in the text, the Ln site is occupied by Y, Ho or Er. $B(\text{nm}^2)$ is the equivalent isotropic thermal parameter. Numbers in parentheses are estimated standard deviations of the last significant digits.

<table>
<thead>
<tr>
<th>Ln</th>
<th>Y</th>
<th>Ho</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a(\text{nm})$</td>
<td>0.386944(7)</td>
<td>0.384137(8)</td>
<td>0.383588(6)</td>
</tr>
<tr>
<td>$b(\text{nm})$</td>
<td>0.386944(7)</td>
<td>0.386974(8)</td>
<td>0.386701(6)</td>
</tr>
<tr>
<td>$c(\text{nm})$</td>
<td>2.72390(5)</td>
<td>2.72338(7)</td>
<td>2.72222(4)</td>
</tr>
<tr>
<td>$R_{\text{Ba}}$</td>
<td>0.3648(4)</td>
<td>0.3647(5)</td>
<td>0.3653(3)</td>
</tr>
<tr>
<td>$z_{\text{Ba}}$</td>
<td>0.005(2)</td>
<td>0.0030(3)</td>
<td>0.0005(18)</td>
</tr>
<tr>
<td>$B_{\text{Ln}}$</td>
<td>0.0050(18)</td>
<td>0.004(2)</td>
<td>0.0055(16)</td>
</tr>
<tr>
<td>$z_{\text{Cu}(1)}$</td>
<td>0.2125(3)</td>
<td>0.2127(3)</td>
<td>0.2123(2)</td>
</tr>
<tr>
<td>$B_{\text{Cu}(1)}$</td>
<td>0.0047(14)</td>
<td>0.0042(18)</td>
<td>0.0047(13)</td>
</tr>
<tr>
<td>$z_{\text{Cu}(2)}$</td>
<td>0.0615(3)</td>
<td>0.0616(3)</td>
<td>0.0612(2)</td>
</tr>
<tr>
<td>$B_{\text{Cu}(2)}$</td>
<td>0.0052(14)</td>
<td>0.0059(19)</td>
<td>0.0040(12)</td>
</tr>
<tr>
<td>$z_{\text{O}(1)}$</td>
<td>0.145(3)</td>
<td>0.145(4)</td>
<td>0.145(3)</td>
</tr>
<tr>
<td>$B_{\text{O}(1)}$</td>
<td>0.0059(19)</td>
<td>0.006(2)</td>
<td>0.0064(17)</td>
</tr>
<tr>
<td>$z_{\text{O}(2)}$</td>
<td>0.0527(3)</td>
<td>0.0532(4)</td>
<td>0.0522(3)</td>
</tr>
<tr>
<td>$B_{\text{O}(2)}$</td>
<td>0.0063(19)</td>
<td>0.007(3)</td>
<td>0.0050(17)</td>
</tr>
<tr>
<td>$z_{\text{O}(3)}$</td>
<td>0.4474(3)</td>
<td>0.4468(4)</td>
<td>0.4480(3)</td>
</tr>
<tr>
<td>$B_{\text{O}(3)}$</td>
<td>0.0046(18)</td>
<td>0.006(2)</td>
<td>0.0047(16)</td>
</tr>
<tr>
<td>$z_{\text{O}(4)}$</td>
<td>0.2818(4)</td>
<td>0.2817(5)</td>
<td>0.2818(3)</td>
</tr>
<tr>
<td>$B_{\text{O}(4)}$</td>
<td>0.011(2)</td>
<td>0.011(3)</td>
<td>0.0103(19)</td>
</tr>
<tr>
<td>$R_{\text{exp}}$</td>
<td>10.62</td>
<td>9.82</td>
<td>8.37</td>
</tr>
<tr>
<td>$R_{\text{E}}$</td>
<td>6.20</td>
<td>3.98</td>
<td>4.58</td>
</tr>
<tr>
<td>$R_{1}$</td>
<td>5.78</td>
<td>7.35</td>
<td>4.60</td>
</tr>
<tr>
<td>$R_{I}$</td>
<td>3.66</td>
<td>4.69</td>
<td>3.09</td>
</tr>
<tr>
<td>$s$</td>
<td>1.711</td>
<td>2.489</td>
<td>1.827</td>
</tr>
</tbody>
</table>

Table II
Interatomic distances (nm) in LBCO (Ln = Y, Ho and Er) at RT. Integers following multiplication signs (*) are numbers of equivalent bonds.

<table>
<thead>
<tr>
<th>Ln</th>
<th>Y</th>
<th>Ho</th>
<th>Er</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)-O(1) ($x_1$)</td>
<td>0.1841(11)</td>
<td>0.1841(14)</td>
<td>0.1842(10)</td>
</tr>
<tr>
<td>Cu(1)-O(2) ($x_1$)</td>
<td>0.1875(10)</td>
<td>0.1881(13)</td>
<td>0.1878(9)</td>
</tr>
<tr>
<td>Cu(1)-O(4) ($x_2$)</td>
<td>0.1940(15)</td>
<td>0.1940(17)</td>
<td>0.1938(8)</td>
</tr>
<tr>
<td>Cu(2)-O(1) ($x_3$)</td>
<td>0.2285(11)</td>
<td>0.2274(15)</td>
<td>0.228(10)</td>
</tr>
<tr>
<td>Cu(2)-O(2) ($x_3$)</td>
<td>0.1934(13)</td>
<td>0.1935(17)</td>
<td>0.1936(12)</td>
</tr>
<tr>
<td>Cu(2)-O(3) ($x_2$)</td>
<td>0.1949(15)</td>
<td>0.1948(19)</td>
<td>0.1945(14)</td>
</tr>
<tr>
<td>Ba-O(1) ($x_4$)</td>
<td>0.2739(14)</td>
<td>0.2736(17)</td>
<td>0.2738(13)</td>
</tr>
<tr>
<td>Ba-O(2) ($x_4$)</td>
<td>0.2965(10)</td>
<td>0.2958(14)</td>
<td>0.2964(10)</td>
</tr>
<tr>
<td>Ba-O(3) ($x_2$)</td>
<td>0.2957(10)</td>
<td>0.2948(13)</td>
<td>0.2958(9)</td>
</tr>
<tr>
<td>Ba-O(4) ($x_2$)</td>
<td>0.2966(10)</td>
<td>0.2965(13)</td>
<td>0.2972(9)</td>
</tr>
<tr>
<td>Ln-O(2) ($x_4$)</td>
<td>0.2409(5)</td>
<td>0.2417(6)</td>
<td>0.2400(4)</td>
</tr>
<tr>
<td>Ln-O(3) ($x_4$)</td>
<td>0.2386(5)</td>
<td>0.2400(7)</td>
<td>0.2384(5)</td>
</tr>
<tr>
<td>Cu(2)-Cu(2) ($x_1$)</td>
<td>0.3349(14)</td>
<td>0.3358(19)</td>
<td>0.333(12)</td>
</tr>
</tbody>
</table>

Symmetry codes: $x_1: x, 1/2-y, 1/2-z$; $x_2: 1/2-y, 1/2-z$; $x_3: x, y, -z$. 

---

265
DISCUSSION

Fig. 5 shows the 'chemical pressure' dependence of the lattice parameter $a$, $b$, $c$ and unit cell volume, $V$, refined from powder X-ray diffraction. The 'chemical pressure' is evaluated from $V$ using the gradient of $V$ vs $p$ plot under pressure, $\frac{dV}{dp} = -0.0025$ nm$^3$ GPa$^{-1}$. The lattice parameters show linearly decreased against the 'chemical pressure'. A linear rise of $T_c$ using this 'chemical pressure' is $\frac{dT_c}{dp} = 3.79$ K GPa$^{-1}$, it is a little lower than that of under pressure.

![Graphs showing the dependence of lattice parameters and $V$ on pressure](Image)

Fig. 5. Dependence of the X-ray diffraction result of lattice parameters and the unit-cell volume, $V$, on evaluated 'chemical pressure' in LnBa$_2$Cu$_4$O$_8$. The linear lines are least-square fits for the data of LnBa$_2$Cu$_4$O$_8$.

The lattice parameter of HoBa$_2$Cu$_4$O$_8$ from neutron diffraction is very different from the result of X-ray diffraction, and larger than that of YBa$_2$Cu$_4$O$_8$. It is not coincide with the difference of ionic radius of Y$^{3+}$ (0.1019 nm) and Ho$^{3+}$ (0.1015 nm). We assume that the sample of HoBa$_2$Cu$_4$O$_8$ used in neutron diffraction is not good sample, and do not use for the following discussion.

Selected interatomic distances of LnBa$_2$Cu$_4$O$_8$ (Ln = Y and Er) from neutron results under 'chemical pressure' are plotted in fig 6. The Cu(2)-O(1) and Cu(2)-Cu(2iii) are shown as a function of pressure. But these data have large standard deviation, and no clear changing can be observed. It is hardly to explain the result of increasing on $T_c$ through the changing of bond lengths.
Recently, Yamada et al.\textsuperscript{5} calculated the Madelung energies of YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} under high pressure, and they were successful to show that the holes are transferred from the chains to the plain. We also calculate the Madelung energy using our neutron result of LnBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} (Ln = Y and Er). We assigned formal charges of +3 for Y and Er, +2 for Ba, and −2 for O. Holes were distributed between two Cu sites; Cu(1) and Cu(2). That is, the Madelung energy was calculated as a function of \( n(\text{Cu(2)}) \) under the linear constraint: \( n(\text{Cu(1)}) + n(\text{Cu(2)}) = +4.5 \), where \( n(\text{Cu(1)}) \) and \( n(\text{Cu(2)}) \) are the positive charges of the Cu(1) and Cu(2) atoms, respectively.

The \( n_p = n(\text{Cu(2)}) - 2 \) is the number of holes per Cu(2) on the CuO\textsubscript{2} plane. The Madelung energies for YBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} (0.0 GPa) and ErBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} (0.36 GPa) take minima at \( n_p \) values of 0.255 and 0.256, respectively. Δ\( n \) is estimated to be about 0.0028 per 1 GPa, and lower than that of under pressure (0.025 GPa\textsuperscript{−1}).\textsuperscript{5} The change of the number of holes are very small and not to explain the increasing of \( T_c \) according to apply the 'chemical pressure'. The neutron powder diffraction measurements of DyBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} (−0.46 GPa; 'chemical pressure') and more good sample of HoBa\textsubscript{2}Cu\textsubscript{4}O\textsubscript{8} will be made near future.

REFERENCES

NEUTRON SCATTERING STUDY ON THE SPIN DYNAMICS OF THE TWO
DIMENSIONAL SQUARE LATTICE ANTIFERROMAGNET, La2NiO4

Kenji NAKAJIMA, Kazuyoshi YAMADA,* Syoichi HOSOYA, Yasuo ENDOH,
Tomoya OMATA,† Masatoshi ARAI, ‡ Andrew TAYLOR

Department of Physics, Tohoku University, Sendai, Japan
† Department of Physics, Kobe University, Kobe, Japan
‡ Rutherford Appleton Laboratory, Chilton, Didcot, UK

ABSTRACT

The spin dynamics of an S=1, two dimensional (2D) square lattice antiferromagnet, La2NiO4 was studied by neutron scattering experiments in wide energy (E<124meV) and temperature (10K<T<600K) ranges. Below Néel temperature (TN), the spin wave excitations of La2NiO4 are well described by a classical spin wave theory. The nearest-neighbor-exchange coupling constant, the in-plane and the out-of-plane anisotropy constants at 10K were determined to be 28.7±0.7meV, 0.10±0.02meV and 1.26±0.12meV, respectively. Above TN, the 2D spin fluctuation was observed over 600K. The critical slowing down behavior of the fluctuation was observed in the enhancement of the low energy component toward TN. On the other hand, the high energy component is hardly affected by the three dimensional magnetic transition and still exists even at TN as observed in La2CuO4. The spin correlation length and the static structure factor at the 2D zone center were measured and compared with theoretical calculations for 2D Heisenberg antiferromagnets.

INTRODUCTION

Two dimensional (2D) quantum antiferromagnetism attracts a renewed interest since the discovery of the cuprate oxide superconductors. Inelastic neutron scattering experiments on La2CuO4, one of the mother systems of the oxide superconductors, have revealed the anomalous feature of this system such as the 2D spin fluctuation of the large energy scale without divergence of the low energy component even at Néel temperature (TN). The properties are in contrast with those of other 2D magnets such as K2NiF4 or La2CoO4 which show the critical slowing down phenomena toward TN, and the spin dynamics of La2CuO4 is considered to be affected by the strong quantum effect for the spin value S=1/2. The proper comprehension of the spin fluctuation in La2CuO4 requires a theoretical model for a quantum square lattice Heisenberg antiferromagnet (SLHAF). Many theoretical efforts have been made to understand the nature of a quantum 2D-SLHAF. Especially the quantum non-linear sigma (QNLS) model analyses well explain the experimental evidences such as the static and the dynamic structure factors or the temperature dependence of the 2D spin correlation length.

To understand the nature of a quantum 2D-SLHAF more in detail, systematic studies on the microscopic parameters, such as the spin value or the exchange coupling constant are indispensable. In this respect, La2NiO4, where Ni2+ has S=1, is an important materials to
elucidate the quantum effect in the 2D antiferromagnetism, since La$_2$NiO$_4$ belongs to the same family of La$_2$CuO$_4$ and the magnetic properties can be understood essentially as a 2D square lattice antiferromagnet.

Previous works\textsuperscript{10,11,12,13} revealed that both magnetic and crystal structures of La$_2$NiO$_4$-$\delta$ are quite sensitive to the oxygen stoichiometry. Therefore much care in the control of oxygen concentration is required in the studies of La$_2$NiO$_4$.

The stoichiometric La$_2$NiO$_4$ has the crystal structure with orthorhombic symmetry presented by Bma$\bar{b}$ at room temperature as in Fig. 1. The three dimensional (3D) antiferromagnetic long range order develops below $T_N$=328K. The Ni$^{2+}$ spins direct along a-axis in the plane, which is parallel to the antiferromagnetic propagation vector and the rotation axis of the oxygen octahedron. The structural phase transition takes place at $T_S$=70K. Below $T_S$ the crystal structure transforms to the tetragonal phase P4$_2$/nmc or the other orthorhombic phase Pccn.

The Hamiltonian for La$_2$NiO$_4$ can be written by a Heisenberg antiferromagnet model with the in-plane and the out-of-plane anisotropies,

$$H=J\sum_{\langle i,j \rangle} S_i \cdot S_j + \sum_i (K_b S_i^b S_i^c + K_c S_i^c S_i^b),$$

where $J$ is the nearest-neighbor-exchange coupling constant, $K_b$ and $K_c$ are anisotropy parameters corresponding to the in-plane and the out-of-plane modes, and $S_i^b$ and $S_i^c$ are the spin component along b and c-axis, respectively. If intra-plane exchange constant is dominant, the spin wave excitations have the dispersion presented by the momentum transfer from the 2D zone center, $q_{2D}$ only, and have no dispersion perpendicular to the plane. Following to the notation of the space group Bma$\bar{b}$ as in Fig.1, the 2D zone center is parallel to c*-axis and locates at \((n,0,0)\) or \((0,n,0)\) (n:integer). The twin structure allows the coexistence of the equal population of a*-c*- and b*-c*- plane for our configuration. Thus the notation \((h,0)\) hereafter denotes \(1/2[(h,0,0)+(0,h,0)].\)

With inelastic neutron scattering experiments, the long wave length spin wave near the 2D zone center has been studied by G.Aeppli et al.\textsuperscript{14} and T.Frelof et al.\textsuperscript{15} An energy gap at the 2D zone center was observed and the spin wave velocity was estimated. The oxygen concentration dependence of the energy gap and the spin wave velocity were reported. However, the detailed analysis on the anisotropy was not performed and the microscopic parameters were left undetermined. As for the 2D spin fluctuation above $T_N$, there is no report on the stoichiometric system.

In present works, we have studied the spin dynamics of La$_2$NiO$_4$ in wide temperature range (10K<$T$<600K). Two types of the spectrometers were used to achieve the wide energy range ($E$<124meV) measurements. The complete spin wave dispersion relation and the microscopic parameters of this system were obtained. We also observed the 2D spin fluctuation above $T_N$ and measured the 2D spin correlation length and the static structure factor, which were compared with the theoretical calculations using QNL$\sigma$ model analyses.

EXPERIMENTS
Single crystal samples were grown by a floating zone method. For measurements on MARI, as-grown crystals were annealed in the CO2(99.9%) + CO(1%) gas flow at 1100°C for 30 hours. For measurements on TOPAN, crystals were reduced to the stoichiometric oxygen concentration at 1000°C for 4 hours in the mixed CO + CO2 gas flow in which the partial pressure of oxygen (Po2) was controlled to be logPo2 = -11.5 or -12, and the stoichiometry was examined by the iodometric titration method. The details of the sample preparation and the post-growth heat treatment were described elsewhere.13) The chopper spectrometer MARI installed at the pulsed neutron source ISIS in RAL, was used to observe the spin wave excitation near the 2D zone boundary. Five single crystals with the total volume of about 8.6 c. c. were assembled and mounted in a cryostat. Measurements were carried out at 35K.

The low energy side measurements have been performed on the triple-axis spectrometer TOPAN installed at JRR-3M at Tokai establishment of JAERI. A crystal of about 1 c. c. in average volume was used. The (0,0,2) reflection of the pyritic graphite (PG) was used as the monochromator and the analyzer. Also, a PG filter was used to reduce the higher order reflection. A 4He-closed cycle refrigerator or a furnace were used to obtain desired temperature.

**SPIN DYNAMICS IN THE 3D ORDERED REGION (T < T_N)**

Inelastic neutron scattering experiments on MARI have revealed the high energy spin wave excitations up to the 2D zone boundary. In Fig. 2, the observed peak positions for different incident neutron energies are depicted in the q2D-ω diagram. The solid lines in the figure indicate the scan trajectories. One can measure the excitations in wide q2D-ω space with varying the incident neutron energy. We assumed the 2D nature of the excitations, which are confirmed in the latter, and the intensity of different detectors at different scattering angles was summed up at a q2D. The details of this experiments are described in the separate paper.16)

From the results, the excitation energy at the 2D zone boundary is determined to be 124±3meV.

Next, we have measured the low energy excitations near the 2D zone center. In Figs. 3(a) and (b), typical results of the energy scan at the 2D zone center are shown. Two energy gaps corresponding to the in-plane and the out-of-plane modes are seen as two peaks of the spectrum. The data were compared with a classical spin wave theory. With the energy gap at the zone center E_{G}, and the spin wave velocity \hbar c = 2aI, where a is a lattice constant of the basal plane, the dispersion relation can be expressed by a formula

\[ \hbar \omega_{q_{2D}} = \sqrt{\hbar c q_{2D}^2 + E_{Gb}^2} \]

\[ \hbar \omega_{q_{2D}} = \sqrt{\hbar c q_{2D}^2 + E_{Gc}^2} \]

\[ g_b = \frac{1}{2} (1 + \sin^2 \alpha) \]

\[ g_c = \cos^2 \alpha \]

Fig. 2. Peak positions (closed circle or ellipsoid) from different incident energies between 70.6 and 416meV depicted on the corresponding scan. 

[Equation 2]

[Equation 3]

[Equation 4]
where \( k_t \) and \( k_t \) are the incident and the scattering neutron wave numbers, respectively, \( \alpha \) is the angle between a* or b*-axis and \( Q \), and \( \Gamma \) is the inverse magnon lifetime, which is expected to be small when the spin wave is well propagative. The variation of the magnetic form factor of the Ni\(^{2+}\) ion is expected to be weak in \( Q \) region which we are concerned\(^1\) and is taken to be constant here. The amplitude, 
\[
Amp_{b(c)}(\hbar\omega,T),
\]
governs the scattering intensity and can be written as 
\[
(n(\hbar\omega)+1)/\hbar\omega_{b(c)}^2 2Db(c),
\]
where \( n(\hbar\omega) \) is the Bose occupation factor.

The energy spectra at the 2D zone center were analyzed by using eqs. (2)-(4), convoluted with the instrumental resolution function. The width \( \Gamma \) was fixed to be 0.5meV. The spin wave velocity was taken to be 340meV/\( \text{Å} \). This value corresponds to \( J=31 \)meV, which is estimated from the excitation energy at the 2D zone boundary.

In Figs. 3(a) and (b), fit results are indicated as the solid lines. The excitation energies at the 2D zone center for the in-plane (ip) and the out-of-plane (op) modes are 7.9±0.6meV and 16.2±0.5meV, respectively, at 80K. At 7S, energy gaps, especially the in-plane gap decrease. At 10K, the excitation energies are 4.1±0.4meV (ip) and 15.7±0.6meV (op). The temperature evolution of the energy gaps deduced from fits are shown in Fig. 4.

Several scans were performed with varying \( f \). The obtained energy gaps are depicted in Fig. 6(b). All the data show no \( f \) dependence within the experimental error. This fact indicates that the 2D nature is dominant in the spin wave excitations. The spectra at \( T<T_\text{S} \) are shown in Fig. 3(b). The solid lines in the figure represent fits results where the overall intensity scale factors are fixed to be same value. The change of the intensity ratio of two peaks is accounted by the change of \( g_b \) and \( g_c \) only. Therefore, the lower and higher energy gaps surely correspond to the in-plane and the out-of-plane modes, respectively.

Then we have performed scans across the 2D zone center with the fixed energy transfer. In Fig. 5, typical results of scans at different energy transfers and at different temperatures are shown. Well resolved spin wave dispersion surface can be observed at higher energy transfer, especially at 35meV.
Data were fitted with a classical spin wave prediction again. The width $\Gamma$ was fixed to be 0.5meV. The instrumental resolution function was convoluted and measured energy gaps were included.

Fits on the higher energy transfer (≥21meV) data, where the dispersion surface is resolved, yield the spin wave velocity to be 320±10meV·Å at 10K. The value well agrees with the previous results. Peak positions resulted from fits are depicted in Fig. 6(a) as hatched circles. The spin wave velocity obtained from fits has rather large uncertainty, therefore, fits were performed again with the fixed spin wave velocity, $\hbar c=340$meV·Å. The solid lines in Fig. 5 indicate the results of fits where the overall intensity scale factor was fixed at the calculated value of the data of $\Delta E=18$meV at $T=10K$. At low temperature, the intensity and the profile of the data are well accounted by a conventional spin wave theory. As temperature approaching to $T_N$, the deviation between measured and calculated spectra becomes appreciable.

The resulted spin wave dispersion is shown in Figs. 6(a) and (b).

Within the linear spin wave approximation, the dispersion relation for Hamiltonian eq.(1) can be written,\(^\text{(18)}\)

$$\hbar \omega_{q_0} = 4JS \sqrt{(1+A)^2 - (\gamma_q B)^2},$$  \hspace{1cm} (5)

$$\gamma_q = \cos \frac{2q}{2D}, A = \frac{1}{4J} (K_b + K_c), B = \frac{1}{4J} (-K_b + K_c).$$

The solid lines in Fig. 6(a) represent the calculation of eq. (5) with $J=31$meV, $K_b=0.032$meV and $K_c=0.52$meV. The obtained dispersion relation well described by the linear spin wave approximation.

For more rigorous treatment, the renormalization for the interaction between spin waves should be accounted. A first order of 1/2S correction after Oguchi\(^\text{(19)}\) is already calculated in literature.\(^\text{(18)}\) We get the renormalized parameters, $J=28.7±0.7$meV, $K_b=0.10±0.02$meV and $K_c=1.26±0.12$meV at 10K.

**SPIN DYNAMICS IN THE 2D REGION ($T\geq T_N$)**

In Fig. 7, the results of the same scans as in Fig. 5 but above $T_N$ are shown. Clear signals are observed over 600K. The temperature evolution of integrated intensities of constant-$E$ scans at several energy transfers are depicted in Fig. 8. In the figure, one can clearly see the
characteristic behavior of the 2D spin fluctuation of this system. The critical slowing down phenomena of the fluctuation is observed in the enhancement of the low energy component toward $T_N$. The high energy fluctuation, however, hardly affected by the 3D magnetic transition. As observed in La2CuO4, the high energy scale of the 2D spin fluctuation even at $T_N$.

Utilizing two-axis scans, one can measure the static structure factor $S(q_{2D})$ and the inverse correlation length $\kappa$. The details of this experimental technique are described elsewhere. Temperature dependence of the inverse correlation length $\kappa$ and the static structure factor at the 2D magnetic zone $S(0)$ are plotted in Figs. 9(a) and (b). The lines in the figures are calculation using QNL$\sigma$ model analyses by Chakravarty, Halperin and Nelson (CHN) and Hasenfratz and Niedermayer (HN). These calculated lines are well explain $\kappa$ and $S(0)$ of this system. Some parameters which are used in calculations, however, should be modified to fit the theoretical prediction with the obtained data. These modifications in parameters are mentioned in the following section.

**DISCUSSION**

Below $T_N$, at low temperature, the spin wave excitations of La2NiO4 are well described by a classical spin wave theory. The system has two energy gaps at the 2D center corresponding to the in-plane and the out-of-plane anisotropies. Also,
In $\text{La}_2\text{CuO}_4$, the excitation energies at the 2D zone center are reported to be 2.8meV and 5.5meV at 8K,\textsuperscript{21} which are rather small in comparison with those of $\text{La}_2\text{NiO}_4$. The large difference in the anisotropies is assumed to be due to the difference of the 3d metal, especially the spin value. It is considered that the anisotropy of $\text{La}_2\text{NiO}_4$ is a single ion type one which is active for $S=1$ and is inactive for $S=1/2$, where the origin of the anisotropy is an anisotropic exchange interaction in $\text{La}_2\text{CuO}_4$. Since the anisotropy of $\text{La}_2\text{NiO}_4$ is mainly a single ion one, it is very sensitive to the local symmetry around Ni$^{2+}$ ion. According to the recent structural analysis by Rodríguez-Carvajal et al.,\textsuperscript{10} the local symmetry of the NiO$_2$ plane changes from lower one to higher one at $T_S$ with decreasing temperature. That is responsible to the change of the in-plane energy gap in $\text{La}_2\text{NiO}_4$.

The 2D spin correlation length and the static structure factor are well agree with the QNL$\sigma$ model analyses. But, corrections should be needed in parameters which are used in calculations. Parameters which are obtained by fits are listed in Table I. In the table, parameters used for $\text{La}_2\text{CuO}_4$\textsuperscript{3,9} and $\text{K}_2\text{NiF}_4$\textsuperscript{22} are listed together. The QNL$\sigma$ analyses predict smaller correlation length for expected parameter sets in the case of $S=1$. Therefore, smaller values of the prefactor $2\pi C_z$ or the spin stiffness constant $2\pi \rho_0$ should be required for $\text{La}_2\text{NiO}_4$ and $\text{K}_2\text{NiF}_4$. One should note here, the same values of $2\pi C_z$ are obtained for $\text{La}_2\text{NiO}_4$ and $\text{K}_2\text{NiF}_4$. The QNL$\sigma$ analyses can be extended to the $S=1$ system. The theoretical understanding for these modification of parameters is highly desirable.

The 2D spin fluctuation of $\text{La}_2\text{NiO}_4$ has the large energy scale even at $T_N$ as observed in $\text{La}_2\text{CuO}_4$. On the contrary to these systems, in $\text{K}_2\text{NiF}_4$ or $\text{La}_2\text{CoO}_4$, the fluctuation is condensed to the quasielastic component toward $T_N$. The difference between $\text{La}_2\text{CuO}_4$ and $\text{K}_2\text{NiF}_4$ can be considered as following.\textsuperscript{3} In $\text{La}_2\text{CuO}_4$, the influence of the anisotropy on the spin dynamics is weak enough near $T_N$, and the 2D spin fluctuation can be a 2D Heisenberg one even at the critical region. According to CHN\textsuperscript{7}, the characteristic energy scales $\kappa^1$ for a 2D Heisenberg model. On the other hand, the 3D magnetic transition in $\text{K}_2\text{NiF}_4$ is driven by the Ising anisotropy, and the critical behavior is that of a 2D Ising model. In this case, the characteristic energy scale is expected to have the lager power dependence on the inverse correlation length like $\kappa^2$. In the region where $\kappa^2 > 1$, the difference of the energy scale becomes about 1000. The same logic can be taken for the case of $\text{La}_2\text{NiO}_4$. In $\text{La}_2\text{CuO}_4$ and $\text{La}_2\text{NiO}_4$, the large energy scale of the 2D spin fluctuation at $T_N$ is considered to be the results of a 2D Heisenberg behavior.

On the analogy of $\text{K}_2\text{NiF}_4$, the Ising like anisotropy is expected in $\text{La}_2\text{CoO}_4$. But the details of the spin dynamics of $\text{La}_2\text{CoO}_4$ is still unknown. Our neutron scattering studies have revealed the spin dynamics of $\text{La}_2\text{NiO}_4$ in wide temperature range, and, now, we have detailed information of the spin dynamics of the 2D-SLHAF with $S=1/2$ ($\text{La}_2\text{CuO}_4$ and $S=1$ ($\text{La}_2\text{NiO}_4$). Our next attention is on the $S=2/3$ system, $\text{La}_2\text{CoO}_4$, and the study of this system is in progress.

<table>
<thead>
<tr>
<th>spin wave theory</th>
<th>fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>$\lambda$(meV)</td>
</tr>
<tr>
<td>CHN</td>
<td>HN</td>
</tr>
<tr>
<td>L$_2$CuO$_4$</td>
<td>1/2</td>
</tr>
<tr>
<td>L$_2$NiO$_4$</td>
<td>1</td>
</tr>
<tr>
<td>K$_2$NiF$_4$</td>
<td>1</td>
</tr>
</tbody>
</table>

Permanent address: Institute for Materials Research, Tohoku University, Sendai, Japan
REFERENCES

21) B. Keimer, R. J. Birgeneau, A. Cassanho, Y. Endoh, M. Greven, M. A. Kastner and G. Shirane: preprint
POLARIZED NEUTRON SCATTERING STUDY OF $\beta$-Mn

Masaayuki SHIGA,* Hiroyuki NAKAMURA,* Masakazu NISHI* and Kazuhisa KAKURAI*

Department of Metal Science and Technology,
Kyoto University,
Kyoto 606-01, Japan

*The Institute for Solid State Physics,
The University of Tokyo,
Tokyo 106, Japan

ABSTRACT

It has been considered that $\beta$-Mn is a Pauli paramagnet without any magnetically ordered state down to 0 K. However, there is much experimental evidence implying the existence of giant spin fluctuations. In this study, we report the results of polarized neutron scattering experiments on a polycrystalline $\beta$-Mn sample performed using a triple-axis spectrometer attached to JRR-3 of JAERI. Measurements were done at room temperature and at 7 K in a constant energy scan mode with $\Delta E = 0$ and 10 meV. In order to know the energy spectrum of spin fluctuations, the constant $Q$ scans were carried out at $Q = 1.6 \AA^{-1}$ and 2.2 $\AA^{-1}$. In the constant $E$ mode, a large scattering centered at $Q = 1.5 \AA^{-1}$ was observed at 290 K, indicating the existence of strong spin fluctuations with antiferromagnetic correlations. This scattering was also observed even at 7 K although the intensity is a little smaller. A constant $Q$ scan with $Q = 1.6 \AA^{-1}$ was performed at both the temperatures. The energy spectrum at 290 K is symmetric but, at 7 K, the scattering is observed only on the energy loss side. The maximum scattering was observed at $\Delta E = 10$ meV. These observations indicate that large zero-point spin fluctuations with antiferromagnetic correlation exist at the ground state.

INTRODUCTION

Manganese metal exhibits interesting properties in many respects. It crystallizes in four allotropic modifications $\alpha$-, $\beta$-, $\gamma$- and $\delta$-phases. The stable phase is $\alpha$, which belongs to b.c.c. Bravais lattice and has a complicated unit cell with 58 atoms. $\beta$-Mn belongs to the simple cubic Bravais lattice with 20 atoms in an unit cell, which divided into two different atomic sites as shown in Fig. 1. The $\beta$-phase exists between 1000 K and 1370 K as the equilibrium state but it is possible to retain this structure down to low temperature by rapid quenching. Other two high temperature phases, $\gamma$ and $\delta$, have f.c.c. and b.c.c. structures, respectively. They are not obtained at low temperatures without adding a second element. Only $\alpha$-Mn has a magnetically ordered state of complicated antiferromagnetic alignment, whose Néel temperature is 100 K. The magnetic moment of Mn takes different values depending upon their atomic sites. The average value is about 0.6 $\mu_B$, which is rather small compared with the number of unoccupied states of 3d bands of about 4 holes per atom. On the other hand, $\beta$-Mn does not order magnetically down to very low temperatures, say 1.4 K. The magnetic susceptibility is nearly constant, indicating the absence of local magnetic moment on Mn atoms. The susceptibility of $\gamma$- and $\delta$-Mn increases slightly with increasing temperature, also indicating absence of local moment in the
naive picture of magnetism. As a whole, it seems that pure Mn is not strongly magnetic: it has a small moment only in the α-phase but has no local moment in other phases.

![Crystal structure diagram](image)

**Figure 1** The crystal structure of β-Mn. Open and solid marks correspond to different crystallographic sites.

On the other hand, it is worthwhile noting that the cohesive energy of 3d transition metals exhibits a strong dip at Mn which locates at the center of 3d series. This behavior is in contrast to 4d and 5d series, which show the maximum cohesive energy at the center of periodic table where a half of d bands is occupied by electrons. The small cohesive energy of Mn may be ascribed to the magnetic effect. In other words, due to the strong electron-electron correlation, 3d-bands are magnetically polarized and one of a plus- or minus-spin band is fully occupied by electrons and the other is empty\(^2\). This interpretation seems, however, contradictory to the apparent absence of magnetic moments. It is possible, however, that the 3d-bands effectively polarize as strong spin fluctuations even at low temperatures. There is much evidence which indicates the existence of strong spin fluctuations in β-Mn. First, the low temperature specific heat is strongly enhanced. The γ-value is as large as 60 mJ/K²mol\(^3\), which is about 7 times of the calculated value for the density of state at the Fermi level\(^4\). Second, the temperature dependence of nuclear spin relaxation rate is well described by the spin fluctuation theory for nearly antiferromagnetic metals\(^5\). In this study, we intend to observe the spin fluctuations in β-Mn by neutron inelastic scattering.

**EXPERIMENTS**

In order to obtain β-phase manganese, an ingot of pure Mn was quenched into iced water from 900 °C. The ingot was prepared by a melting of 99.96 % pure electrolytic Mn in an induction furnace for outgassing. The quenched ingot was crushed into coarse powder for X-ray
and neutron scattering measurements. No other phase than $\beta$ was detected by X-ray diffraction measurement.

Polarized neutron scattering measurements were performed using a triple axis spectrometer attached to JRR-3 of JAERE (5G PONTA). Both the constant $E$ and the constant $Q$ scan modes were carried out at room temperature and 7 K. Throughout the present measurements, the incident neutron energy of 80 meV was used. Energy resolution of the spectrometer was set to $\approx$10 meV.

In order to calibrate the intensity and the polarization rate, quasi elastic scattering of the (221) nuclear Bragg peak was measured in the same condition as polarization analyses in various modes of guide fields and spin flipper. Raw count rates for vertical and horizontal guide fields and for flipper-off and -on conditions were analyzed to obtain the magnetic scattering rate according to a method described in Ref. 6.

![Graph of β-Mn (221) peak with data points for vertical and horizontal fields.](image)

**Figure 2** The (221) nuclear Bragg peak of β-Mn measured in vertical and horizontal guide fields and at room temperature. Open and solid circles indicate the data with spin flipper on and off, respectively.
RESULTS

Figure 2 shows the (221) nuclear Bragg peak measured in the same condition as polarization analyses. From these spectra, we obtained polarization rates $R = I^+ / I^- = 19.5$ and $20.3$ for vertical and horizontal guide fields, respectively.

![Figure 2](image)

Figure 3 Neutron scattering spectra of $\beta$-Mn as a function of wave vector $Q$ measured in the constant $E$ mode with the energy transfer $\Delta E = 0$. Solid and open circles indicate the results at room temperature and at $7\,\text{K}$, respectively.

![Figure 3](image)

Figure 4 Neutron scattering spectrum of $\beta$-Mn as a function of wave vector $Q$ measured in the constant $E$ mode with the energy transfer $\Delta E = 10\,\text{meV}$ and at $7\,\text{K}$.

![Figure 4](image)
Figure 3 shows the result of the constant E scan of β-Mn at room temperature and 7 K for zero energy transfer, ΔE = 0. The count rate is proportional to the squared amplitude of spin fluctuations with the wave number Q and the specific energy within 10 meV. A broad peak was observed around Q = 1.5 Å⁻¹. This wavelength corresponds to approximately twice of the mean inter-atomic distance, indicating the existence of spin fluctuations with antiferromagnetic correlation. The amplitude decreases with decreasing temperature. However, it is worthwhile

![Graph (a)](image)

**β-Mn**

40°-80°-80°-80°

k₁ = 6.2087 Å⁻¹

Q = 1.6 Å⁻¹

![Graph (b)](image)

**β-Mn**

40°-80°-80°-80°

k₁ = 6.2087 Å⁻¹

Q = 2.2 Å⁻¹

Figure 5 Neutron scattering spectra of β-Mn as a function of energy transfer ΔE measured in the constant Q mode with the wave vectors Q= 1.6 Å⁻¹ (a) and 2.2 Å⁻¹ (b). Solid and open circles indicate the results at room temperature and at 7 K, respectively.
noting that the scattering was still observed even at 7 K. A sharp peak at \( Q = 1.2 \ \text{Å}^{-1} \) of the spectrum at 7 K may be ascribed to spin reversal scattering associated to the (1/2 1/2 1/2) magnetic peak of antiferromagnetic MnO impurities by the following reasons: 1) The peak position exactly corresponds to the (1/2 1/2 1/2) Bragg reflection of MnO. 2) This peak was not observed at room temperature which is higher than \( T_N \) of MnO. 3) It is likely that the sample was partially oxidized during experiments.

Figure 4 shows the results of the constant \( E \) scan for energy transfer of 10 meV at 7 K. The profile of the spectrum is not remarkably different from that for \( \Delta E = 0 \). It looks a little broader than that for \( \Delta E = 0 \). It should be noted that the peak at 1.2 Å\(^{-1} \) disappears, again supporting a previous interpretation for the origin of this peak.

Figures 5 a) and b) show the results of the constant \( Q \) scan for \( Q = 1.6 \ \text{Å}^{-1} \) and \( Q = 2.2 \ \text{Å}^{-1} \). The former wave number corresponds to the peak position of the constant \( E \) (\( \Delta E = 0 \)) scan. Therefore, the count rate is proportional to the energy spectrum of antiferromagnetic spin fluctuations. At 7 K, scatterings are observed only on the energy loss side of the spectrum (\( \Delta E > 0 \)), indicating the absence of thermal spin fluctuations and the existence of notable zero-point spin fluctuations whose energy distribution is fairly wide.

**DISCUSSION**

The spin fluctuations in \( \beta \)-Mn observed by the present neutron scattering measurements may be characterized in the following: 1) They exhibit antiferromagnetic correlation. 2) The amplitude of spin fluctuations decreases with decreasing temperature. 3) However, zero-point fluctuations remain even at the lowest temperature. These characteristics are very similar to the behavior observed in the \( Y_{0.97}Sc_{0.03}Mn_2 \) compound\(^7\), although the absolute value of the amplitude of fluctuations cannot be directly compared because of the difference in width of the energy window. A preliminary analysis for the scattering amplitude of the present results gives the equivalent Bohr magneton number of the peak value to be 0.2, which is smaller than that of \( Y_{0.97}Sc_{0.03}Mn_2 \) by almost one order. Noting, however, the narrow width of the energy window and the energy spectrum of \( \beta \)-Mn, which shows a maximum at around 10 meV (Fig. 5a), it is likely the integrated amplitude of spin fluctuations of \( \beta \)-Mn is comparable with that of \( Y_{0.97}Sc_{0.03}Mn_2 \).

Noting the giant amplitude of quantum (zero-point) fluctuations with antiferromagnetic correlation at low temperatures, we have claimed that the ground state of \( Y_{0.97}Sc_{0.03}Mn_2 \) can be regarded as quantum spin liquid\(^8,9\). Studying effects of the substitution of nonmagnetic impurity such as Al for Mn on magnetic and other properties, we have shown that the spin liquid state is realized as a result of the frustration of magnetic interactions and the substitution of nonmagnetic impurities disturb dynamical spin fluctuations, giving rise to a spin-glass state\(^9\). It has been shown that the Mn moments on Cu sites of the \( \text{MgCu}_2 \) type Laves phase structure (C15) interacting with nearest neighbor antiferromagnetic exchange integrals construct a fully frustrated system, having a macroscopic number of degeneracy of spin configurations and, therefore, they can not form a stable antiferromagnetic ordered state\(^10\) but condense into a nonmagnetic ground state, possibly like a quantum spin liquid state\(^11\). We may say that the \( \beta \)-Mn structure is constructed by connecting deformed tetrahedrons of Mn atom as shown in Fig. 1. Therefore, it is likely that \( \beta \)-Mn is more or less in a magnetically frustrated state. Actually, studying magnetic and other properties of the \( \beta \)-Mn\(_{1-x}\)Al\(_x\) system, we have shown that effects of Al substitution for Mn are almost same with those for the \( Y(Sc)(\text{Mn})_1\)Al\(_2\) system\(^12\), namely, 1) the temperature dependence of susceptibility exhibits a sharp maximum for \( x > 0.5 \), 2) the electronic specific heat coefficient, the \( \gamma \)-value, decreases rapidly with increasing x, 3) the temperature dependence of electrical resistivity becomes nearly constant over a wide temperature range. These drastic changes can be understood as the results of spin-liquid to spin-glass transformation caused by the substitution of nonmagnetic impurities for the fully frustrated system, because the nonmagnetic impurities partially raise the degeneracy of spin configurations in the pure system.
In conclusion, the ground state of $\beta$-Mn may be regarded as a quantum spin liquid state, which is characterized by the existence of large amplitude of zero-point spin fluctuations with antiferromagnetic correlation. Such a particular state may be realized as a result of the magnetic frustration. The low cohesive energy of manganese could be ascribed to the existence of strong spin fluctuations in quantum and thermal natures.

ACKNOWLEDGEMENT

The authors are indebted to Dr. H. Wada and Dr. K. Motoya for helpful discussion. They are also grateful to Mr. R. Iehara for his technical support and to Messrs. K. Yoshimoto, T. Suzuki and T. Yaegashi for assistance in measurements.

REFERENCES

NEUTRON DIFFRACTION STUDY AND MAGNETIC PROPERTIES OF La$_2$NiO$_{4+x}$

*Nobuyoshi YAMADA, *Naoki TAKADA, **Satoru FUNAHASHI and *Kay KOHN

*Department of Applied Physics and Chemistry,  
University of Electrocommunications  
Chofu-shi, Tokyo 182 Japan

*Department of Physics,  
Waseda University  
Shinjuku-ku, Tokyo 169 Japan

**Division of Physics, JAERI,  
Tokai-mura, Ibaraki 319-11 Japan

ABSTRACT

We reported the dependence of the magnetic properties of La$_2$NiO$_{4+x}$ (x=0.05 and 0.1) on the amount of the excess oxygen in the temperature range below 60 K. Weak ferromagnetic moment having spin glass like features was observed in the both compounds. La$_2$NiO$_{4+0.1}$ showed the shifted magnetization curve. These magnetic features were explained with the two-phase model: that is, there are two magnetic regions (the one phase is of nearly stoichiometric La$_2$NiO$_4$ which has the weak ferromagnetic moment, and the other is of antiferromagnetic La$_2$NiO$_{4+x}$ with excess oxygen). They interact with each other in the boundary region. The neutron diffraction patterns of both specimens were refined using Rietveld analysis with two-phase model (F4/mmm+Fccm, at 15 K, and F4/mmm+Bmab, at 293 K).

INTRODUCTION

The layered perovskite La$_2$NiO$_4$ has been a subject of numerous studies on account of its structural similarity to the high temperature superconducting oxide La$_2$CuO$_4$. Spalek et al.$^{13}$ observed the diamagnetic behavior in La$_{1.8}$Sr$_{0.2}$NiO$_4$ below 20K, and claimed to be the evidence of superconductivity in this oxide.

The magnetic properties of La$_2$NiO$_4$ have been discussed in a number of papers based on the magnetic as well as neutron diffraction studies.$^{3-15}$ Their results show that the
magnetic properties of La$_2$NiO$_{4+x}$ change their character depending on the oxygen stoichiometry and probably on the homogeneity of the sample studied. The results of different studies are quite different and sometimes contradictory with each other, probably because of difference in their samples.

The recent neutron diffraction studies seem to reach the essentially same conclusion that the stoichiometric La$_2$NiO$_4$ specimen have the three-dimensional antiferromagnetic order below T$_N$, which is higher than 300 K and that the magnetic moment of Ni is along the a axis of the orthorhombic cell. One of the problem on controversy is the origin of a small spontaneous magnetization observed at low temperatures and its relation to the structure. Yamada K. et al. discussed the magnetic properties and the crystal structure, and then reported that the spontaneous magnetization exists only below 70 K, where a structure phase transition occurs. Rodríguez-Carvajal et al. discussed the possible spin structures in the space groups Bmab, Pccn and P4$_2$/ncm, based on the macroscopic theory of spin configurations (E. F. Bertaut). Then they concluded that the canted spin configuration could not exist in the Bmab phase and be allowed in the P4$_2$/ncm (or Pccn) phase. For La$_2$NiO$_{4+x}$ with excess oxygen content x in between 0.02 and 0.13, the system was reported to separate into two phases with different oxygen defect concentrations by Jorgensen et al. and Rodríguez-Carvajal. The coexistence of the magnetic two phases with and without spin canting was pointed out by Yamada K. et al.

In the present paper we report the results of neutron diffraction and magnetic studies of the powder samples of La$_2$NiO$_{4+x}$ with a definite oxygen stoichiometry (x=0.05 and 0.10). Our main concern is the relation between the weak ferromagnetic moment observed in oxygen-excess La$_2$NiO$_4$ and its structure, particularly the some structural disorders affecting weakly ferromagnetic properties.

**EXPERIMENTAL**

We prepared two different powder samples A and B by a standard ceramic method from the mixture of stoichiometric amount of NiO and La$_2$O$_3$ powder. The mixture was ground thoroughly, pressed, and sintered at 1050 °C in air two times before the final heat treatment. Its condition was;

(1) annealing at 1100 °C for 20 hrs in air followed by furnace cooling (the sample A, x = 0.05), or
(2) annealing at 900 °C for 20 days in a sealed tube (the sample B, x = 0.10).

The amount of excess oxygen x was determined with thermogravimetry, in which the sample was reduced to metallic Ni and La$_2$O$_3$ in Ar/H$_2$ flow. They were identified as composed only of single phase of K$_2$NiF$_4$ type La$_2$NiO$_{4+x}$ with X-ray powder diffraction. The lattice parameters a, b and c determined at the room temperature were in good agreement with the values by the neutron diffraction study.

Magnetization measurements was made with a vibrating sample type magnetometer (PAR 4500). The sample temperature was detected with a calibrated AuFe–AuAg thermocouple. The magnetic field applied on the sample was less than 50 Oe, during the zero field cooling and the remenance measurements.

Neutron diffraction data were collected using a high resolution powder diffraction spectrometer at the JRR–3 reactor of the Japan Atomic Energy Research Institute, Tokai. The neutron diffraction wave length was 1.8225 Å. The measurement was made on the powder specimen contained in an aluminum container at temperatures 15 and 293 K. The
crystal structures were refined by Rietveld analysis using a program package RIETAN.\textsuperscript{17)} The crystal structure refinement were made based on the two-phase-mixture model according to Rodríguez-Carvajal: that is, for 15 K, \textit{P4$_2${}n}$_{ncm}$+\textit{F4}$_{mmm}$ or \textit{Pccn}+\textit{F4}$_{mmm}$, and for 293 K, \textit{Bmab}+\textit{F4}$_{mmm}$. The effect of the microstrain induced by the interstitial oxygens was not taken into account explicitly, but the parameters for the line width of \textit{F4}$_{mmm}$ were refined and these for \textit{Bmab}, \textit{P4$_2${}n}$_{ncm}$ and \textit{Pccn} phase were fixed to the values expected from the instrumental situations.

RESULTS

Both the samples exhibited small spontaneous magnetization at 4.2 K, when they had been cooled down in magnetic field. The magnetization curves at 4.2 K are shown in Figures 1 and 2. The sample A showed a well saturated hysteresis curve characteristic of a parasitic weak ferromagnet. On the while, the sample B with much more excess oxygen showed a rather linear magnetization curve which was shifted toward the positive (parallel to the field during cooling) magnetization. It could not be saturated within the field up to 20 kOe. The remanent magnetization of the samples A and B disappeared at about 35 K and 40 K, respectively.

Both the samples showed relaxation phenomena typically observed in spin glasses. They are;

(1) The temperature dependence of the magnetization at a fixed magnetic was dependent on whether the sample was field-cooled or zero-field-cooled, and
(2) The thermoremanent magnetization (TRM) had also a characteristic temperature dependence during heat cycles. Figure 3 shows the dependence of thermoremanent magnetization for the sample B on heat cycles. The TRM decreased irreversibly with rising of temperature, and, however, it remained almost at the same level and changed reversibly with the heat cycles, when the sample was cooled down from a certain temperature and then heated up in zero magnetic field.

These magnetic relaxation phenomena indicate that the local magnetic moments of various parts of a sample is freezed in different directions during cooling. Nimori et al.\textsuperscript{11)} also reported a decay of remanent magnetization in a single crystal of \textit{La$_2$NiO$_{4+x}$}.

Figure 4 shows the observed neutron diffraction data taken at 15 K and 293 K by dots together with the calculated curve after refinement. The final values of structure parameters were listed in the Table I. Table II shows the estimated fraction of each phases. We could obtain rather small reliability factor when we refined the patterns at 15 K with \textit{Pccn}+\textit{F4}$_{mmm}$ phases than with \textit{P4$_2${}n}$_{ncm}$+\textit{F4}$_{mmm}$ phases. However, in order to claim the superiority of the \textit{Pccn} phase to the \textit{P4$_2${}n}$_{ncm}$ phase, there must be further experiments. Nevertheless, we can say that we must refine the neutron diffraction patterns with the two-phase model rather than with a single phase model.
Figure 1. Magnetization curve of polycrystalline La$_2$NiO$_{4.05}$(the sample A) at 4.2 K.

Figure 2. Magnetization curve of polycrystalline La$_2$NiO$_{4.10}$(the sample B) at 4.5 K.

Figure 3. The dependence of thermoremanent magnetization for the sample B on temperature cycles. The direction of the temperature change during the measurement is shown by arrows.
Figure 4. Neutron diffraction data and the result of Rietveld analysis of $\text{La}_2\text{NiO}_4\text{O}_8$ at 15 K. The observed data are indicated by dots and the calculated pattern is shown by solid line. The vertical marks in the central portion show the calculated angular positions of diffraction lines. The upper and lower vertical marks were of $\text{Pce}1$ and $\text{F}4\text{mmm}$, respectively. The lower portion is plots of the difference between the observed and calculated intensities.
Table I
Refined parameters of Rietveld analysis for each phase in La$_2$NiO$_{4.05}$ at 15 K.

Rwp=9.70%, Re=3.18%

$F4/mmm$: Abundance 90%
$a=b=5.4491(8)$ Å, $c=12.629(2)$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>n</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2</td>
<td>8e</td>
<td>0</td>
<td>0</td>
<td>0.3602</td>
<td>0.11</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.51</td>
</tr>
<tr>
<td>O1</td>
<td>2</td>
<td>8c</td>
<td>1/4</td>
<td>1/4</td>
<td>0</td>
<td>0.89</td>
</tr>
<tr>
<td>O2</td>
<td>1.8</td>
<td>8e</td>
<td>0</td>
<td>0</td>
<td>0.1726</td>
<td>2.30</td>
</tr>
<tr>
<td>O1</td>
<td>0.05</td>
<td>-</td>
<td>1/4</td>
<td>1/4</td>
<td>0.242</td>
<td>1</td>
</tr>
<tr>
<td>OD</td>
<td>0.2</td>
<td>-</td>
<td>-0.062</td>
<td>-0.062</td>
<td>0.172</td>
<td>1</td>
</tr>
</tbody>
</table>

R$_1$ = 5.2%

$Pccn$: Abundance 10%
$a=5.4357(9)$ Å, $b=5.4628(10)$ Å, $c=12.615(2)$ Å

<table>
<thead>
<tr>
<th>Atom</th>
<th>n</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2</td>
<td>8f</td>
<td>0.0003</td>
<td>-0.0062</td>
<td>0.3594</td>
<td>0.11</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.51</td>
</tr>
<tr>
<td>O1</td>
<td>2</td>
<td>8c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.0078</td>
<td>0.89</td>
</tr>
<tr>
<td>O2</td>
<td>2</td>
<td>8f</td>
<td>0.0004</td>
<td>0.0260</td>
<td>0.1721</td>
<td>2.30</td>
</tr>
</tbody>
</table>

RI = 4.98%

Table II
Abundance of each phase in La$_2$NiO$_{4.4}$.

Abundance(%)  

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Space group</th>
<th>15 K</th>
<th>293 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(F4/mmm+)</td>
<td>Pccn</td>
<td>P4$_2$/nmc</td>
</tr>
<tr>
<td>Sample A</td>
<td>La$<em>2$NiO$</em>{4.05}$</td>
<td>F4/mmm</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bmab</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pccn</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P4$_2$/nmc</td>
<td>–</td>
</tr>
<tr>
<td>Sample B</td>
<td>La$<em>2$NiO$</em>{4.10}$</td>
<td>F4/mmm</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bmab</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pccn</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P4$_2$/nmc</td>
<td>–</td>
</tr>
</tbody>
</table>
DISCUSSION

The magnetization curve of the sample A at 4.2 K is apparently typical of parasitic weak ferromagnetism accompanied with the antiferromagnetic order. However, there are some features, such as the existence of magnetic relaxation and the gradual disappearance of remanent magnetization, which cannot be directly explained by the concept of parasitic ferromagnetism. Such tendency is more remarkable in the sample B with an unsaturated hysteresis loop.

In principle, the existence of weak ferromagnetic moment is closely connected with by the symmetry of crystal structure. Rodríguez–Carvajal et al.\textsuperscript{14} made it clear that the canting in a widely accepted spin structure is impossible in \textit{Bmab} but possible in \textit{P4}_\textit{mmm} or in \textit{Pccn}. The direction of the moment is determined by the magnetic symmetry of the crystal.

However, real samples of \textit{La}_2\textit{NiO}_4\textsubscript{x} have some structural disorders, particularly oxygen interstitial (or some other point defect due to the excess of oxygen) and the existence of two different phases in our samples. We tentatively take a model that \textit{La}_2\textit{NiO}_4\textsubscript{x} within the two phase region is considered to be composed of small domains of the orthorhombic structure (\textit{Pccn}) of stoichiometric \textit{La}_2\textit{NiO}_4 with parasitic ferromagnetic moment and those of the tetragonal structure (\textit{F4}_\textit{mmm}) with excess oxygen, if it is well annealed. This is supported by the result of our neutron study. If the domains have an appropriate size, the sample is composed of small ferromagnetic particles within non–ferromagnetic matrix. The magnetic behavior of \textit{La}_2\textit{NiO}_4\textsubscript{x+1} can be explained by the exchange interaction between two phases: that is, the small ferromagnetic moments and the antiferromagnetic moments( exchange anisotropy). Randomness of excess oxygen causes a strain on the boundary of the stoichiometric region and thus distributing the magnetic moment of the particles randomly. This is a possible origin of magnetic relaxation phenomena observed in our samples. Of course, we have no experimental evidence about the size and shape of such domains. It is desirable that direct observation by HREM will be performed with oxygen–excess \textit{La}_2\textit{NiO}_4 samples.

Acknowledgements

The authors would like to express sincere gratitude to Professor K. Sekizawa and Mr. K. Ohtani of Nihon University for the thermogravimetric analysis of the samples.
References

9) Yamauchi, Y., T. Fukuda, H. Yamaguchi, S. Hosoya and T. Kajitani.: Read at the Autumn Meeting of the Physical Society of Japan, Kagoshima, October, 1989
NEUTRON SCATTERING EXPERIMENTS ON ANTIREFROMAGNETIC ABX₃ SYSTEMS: STUDY OF THE HALDANE CONJECTURE

Kazuhisa KAKURAI, Toshiya INAMI, Kenji NAKAJIMA¹, Shinichi ITOH¹, Hidekazu TANAKA², Mechthild ENDERLE³, Kurt N. CLAUSEN⁴ and Michael STEINER⁵

Institute for Solid State Physics
University of Tokyo, 106 Tokyo, Japan

¹Department of Physics
Tohoku University, 980 Sendai, Japan

²Faculty of General Education,
Nagoya University, 464-01 Nagoya, Japan

³Institut für Physik,
University of Mainz, D-6500 Mainz, Germany

⁴Department of Solid State Physics
Risø National Laboratory, DK-4000 Roskilde, Denmark

⁵Bereich Strukturforschung
Hahn-Meitner-Institut, D-1000 Berlin, Germany

ABSTRACT

In this contribution we would like to present the results of detailed and comprehensive studies by means of neutron scattering in numerous antiferromagnetic, quasi one-dimensional ABX₃ systems with different spin values. These results support the Haldane conjecture and indicate furthermore the influence of the quantum effects even in the three dimensionally ordered systems.

The quantum nature of low-dimensional(D) antiferromagnetic(AF) systems has been of continuous interest. To name some examples, we mention the rigorous results on the ground-state energy of S=1/2, AF chain by Bethel,¹ the energy calculation of the lowest excited state by des Cloizeaux and Pearson,² and its experimental verification by Endoh et al. in CuCl₂₂N(C₅D₅).³ In this experiment the existence of the spin wave double continuum, predicted by the numerical calculation by Müller et al.⁴, was also indicated. This continuum has been recently verified in KCuF₃ using a chopper instrument at the pulsed neutron source by Nagler et al.⁵ The qualitative resemblance of the energy of the lowest excited state in this extreme quantum S=1/2 case and the classical spin-wave (SW) energy dispersion based on the Néel ordered state besides the energy renormalization led to the often used SW picture even for small S values.

It was therefore very controversial when in 1983 Haldane,⁶ using a field theoretical argument, pointed out the different nature of integer and half-integer spin value
antiferromagnetic systems. It was especially controversial because the extreme quantum nature of the spin value dependence was derived by taking the limit of $S$ to infinity. Among other phenomena Haldane predicted a finite energy gap for the 1-D, integer spin value, isotropic Heisenberg antiferromagnet (HAF) in contrast to the conventional classical SW picture. Subsequently the theoretical controversy seems to have been settled in favour of the existence of the so called "Haldane gap." The study of the exactly solvable model, quantum Monte Carlo calculation and the finite size scaling support the existence of a finite gap for the $S=1$ isotropic HAF system. A search for a physical understanding of the difference between the half integer and integer case has also been initiated invoking the "zero spin defect" picture. Köhler and Schilling applied a self-consistent approach using this zero spin defects to determine the phase-diagram in exchange and crystal field anisotropy space at $T=0$ and finite temperatures. The results are in reasonable agreement with earlier numerical results. Experimental evidence for the Haldane gap has been sought intensively by different techniques. Especially two kinds of systems have been studied very extensively under the aspect of Haldane conjecture: namely organic, quasi 1-D systems, most prominently Ni(N$_2$C$_2$H$_8$)$_2$(NO$_2$)ClO$_4$, abbreviated NENP, and ionic $ABX_3$ systems, here especially CsNiCl$_3$.

Magnetization and susceptibility measurements have been performed on NENP. The vanishing susceptibility towards $T=0$ and the existence of the critical fields in all three crystallographic directions can be understood as the consequences of the Haldane ground state. ESR measurements have been performed on Cu-substituted NENP indicating the substituted Cu S=1/2 ions breaking the "valence bond solid" in the S=1 Ni-chains. The absence of the 3-D order down to $T=0.2K$ shows that NENP is a nearly ideal $S=1$, 1-D system. But the neutron scattering results reveal that it has rather a large planar anisotropy D. In contrast to NENP, $ABX_3$ systems order three dimensionally at finite temperatures due to a weak, but finite interchain coupling. In CsNiCl$_3$ the dispersion relations both below and above 3-D order were studied in detail by inelastic neutron scattering and it was concluded that the observed spin excitations cannot be explained by the classical SW theory. A new concept introduced by Affleck can overcome the difficulties. In this concept the Haldane gap is introduced naturally and the 3-D ordered state can be interpreted as the Haldane state in the ordered phase. This fact is remarkable because so far the opinion has been accepted, that the 3-D ordered state can well be described by the classical SW theory assuming a kind of Néel order of the spin vectors. This is a first indication that quantum effects severely modify the spin excitations in the 3-D ordered state. In opposition to this interpretation there was a different approach by Plumer and Caille suggesting that the peculiarity of the dispersion relations observed in $ABX_3$ systems are related to the frustration inherent to these triangular structures.

To clarify this point and further establish the quantum effect in the $ABX_3$ systems we performed detailed and comprehensive studies by means of inelastic neutron scattering in numerous AF $ABX_3$ systems. In this contribution we compare the results on CsNiCl$_3$($S=1$) and CsMn$_3$($S=5/2$), especially the field dependence of the dispersion. In the latter the classical SW calculation gives an adequate description and proves that the inadequacy of the SW interpretation in the former is indeed due to quantum effects. Some recent results on $S=3/2$ $ABX_3$ system is also presented, which indicate the cross-over behaviour from the quantum to classical nature of the spin excitations.

Experimental Results and Discussions

Triple axis experiments were performed on instruments at the Institut Laue-Langevin(Ill), Risø National Laboratory(RNL) and Japanese Atomic Research Institute(JAERI). The chopper experiment was performed at Rutherford Appleton Laboratory(RAL).

Figure 1 shows the spin excitation branches in CsNiCl$_3$, a $S=1$ AF system with very small Ising like anisotropy, at $Q=(0,0,1)$ as observed using the polarized thermal neutron triple axis
instrument IN20 at ILL. At low applied field both in spin flip (SF) and non-spin flip (NSF) scattering a resolution limited peak at E=0.5THz is observed (fig. 1a). One should note that the classical SW theory predicts three modes with different energies at this Q. The interpretation by Plumer and Caillé implies only a y-polarized mode, i.e. NSF scattering, at this energy. As mentioned in the introduction, the Landau-Ginsburg model proposed by Affleck can explain these results of polarized neutron scattering naturally as reminiscent of the disordered Haldane state.

![Graphs of NSF and SF spectra](image)

Figure 1. (a) NSF and SF spectra at Q=0.0,1 for T=2K and H=0.8T. (b) NSF and SF spectra at Q=0.0,1 for T=2K and H=5.9T. Counts are per 104 monitor counts, corresponding to roughly 22 min. counting time. The full curves are fits with Gaussians. The horizontal bar indicates the instrumental resolution.

![Graph of field dependence](image)

Figure 2. Field dependence of the observed excitation energies at Q=0.1,0.1,1 for 2K. The modes observed in SF and NSF are indicated by open circles and full squares respectively. The solid and broken lines are theoretical predictions for SF and NSF modes respectively after ref. [24].

Applying a field of 5.9T the NSF hardly changes, but the SF scattering clearly splits into two modes (fig. 1b). The SW theory predicts field independent modes with x,z-polarization and a weakly field dependent mode with y-polarization in the experimental field range. This would mean a field independent SF scattering and weakly field dependent NSF scattering, in contrast to the experimental observations. On the other hand the field dependence of the modes near Q=0.0,1 can be qualitatively understood within the frame of the ordered Haldane state as shown by Affleck and Wellmann. Figure 2 shows the field dependence of the spin excitation modes at Q=0.1,0.1,1 as observed with polarized neutrons. The lines indicate
the theoretical predictions by Landau-Ginsburg model. Although the number of so far unobserved modes becomes higher at finite field, the Zeeman-like field-dependence of these three modes are qualitatively reproduced.

The ultimate proof, that these discrepancies to the SW interpretation observed in S=1 system are caused by the quantum effect, is to check the applicability of the SW theory to a similar system with large spin value.

Figure 3a and 3b show the spin excitation branches in CsMnI$_3$, a S=5/2 AF system with Ising like anisotropy, at Q=(0,0,1) and (-1,-1,1) in zero applied field as observed using the cold neutron triple axis instrument TAS7 at RNL.

Clearly three different energy modes are seen in this S=5/2 system. Since the lowest energy mode at 1.0meV is only seen at Q=(-1,-1,1), this mode can be assigned as having a z-polarization. The high energy mode at 1.8 meV is observed at both Q-vectors and since the intensity ratio at these scattering vectors can be well accounted for by the magnetic form factor (ratio ~1.5) and the difference in the effective absorption due to the scattering geometry (ratio ~2.9) we can assign this mode to the y-polarization. The mode at 1.3meV is best observed at Q=(0,0,1) and therefore should be designated as possessing the x-polarization. This sequence of the polarization assignment is in perfect agreement with the classical SW theory.

Figure 3c and 3d show the spectra in an applied field of 4.5T. The most significant field dependence is seen with the mode with highest energy, i.e. the mode with y-polarization. The other x- and z-mode hardly show any field dependence. This findings are again in full agreement with the classical SW predictions.

To follow the dispersion perpendicular to the chain direction energy scans at different (h,h,1) were performed using the thermal neutron triple axis instrument PONTA installed in the reactor hall of JRR-3M at JAERI. Figure 4 shows the results of these scans at several Q values. The solid line is the results of the best fits with the resolution limited gaussian peaks. At Q=(0,0,1) the peak positions obtained from the high resolution measurements were assumed.
Figure 5 displays the fitted peak positions along (h,h,1). The lines are the dispersion predicted by the classical SW theory when the above mode assignments at Q=(0,0,1) and the

Figure 4. Inelastic spectra in CsMnI₃ at different Q=(h,h,1)

zone boundary energy in the chain direction measured in the previous experiment²⁵) are acquired. The microscopic parameters of the Hamiltonian to meet these requirements are J/k_B=−9.5K, J'/k_B=−0.045K and D/k_B=0.042K. The numbers at the lines are the intensities expected from the SW theory and the numbers in the brackets are the observed intensities. One notices a quite good overall agreement even in the intensities. Only the intensity ratio at Q=(0.4,0.4,1) between the high energy mode and the low energy acoustic mode deviates considerably from the prediction.

These results on the SW dispersion in CsMnI₃ clearly demonstrate that the classical SW theory is applicable for the S=5/2 system. Hence the deviation from this classical behaviour in CsNiCl₃, a S=1 system, should be regarded as a consequence of the quantum effect and not a frustration effect as proposed by Plumer and Caillé.²³)
Having demonstrated the importance of the quantum effect in the ordered S=1, AF system, it is of great interest to study the cross-over to the classical limit as represented by the S=5/2 system. Especially in the light of the Haldane conjecture, where different spin dynamics are expected in the integer and half-integer systems, we have chosen CsVC13, a S=3/2 planar AF system, to study this cross-over effect.

In CsVC13 the dispersion along the chain direction was determined applying the time of flight method at pulsed neutron sources. Due to the rather large exchange constant in the chain direction the zone boundary energy is too high to be followed by the conventional triple axis technique.

The sample consisted out of four in c* direction aligned single crystals. The c-axis was oriented along the incident neutron direction. This orientation enabled the use of the small angle detectors (covering 3–13° of scattering angles) for integrating the equivalent q points on the plane perpendicular to the 1-D direction. For one incident energy the time-of-flight (TOF) spectrum gives a cut through 1-D dispersion according to the energy-momentum relationship. Data were taken at T=40K with incident energies of E_i=100,150,200 and 300 meV. For the incident energy of 150 meV background measurement was performed by turning the sample by 90°, i.e. c* perpendicular to k_i. The vertically positioned small angle detectors then measure the zeroth order plane of this 1-D AF systems, hence no magnetic contributions are expected and thus can be regarded as the true background. To avoid this time consuming background measurement for each incident energy, following method is introduced: By comparing the background measurement at E_i=150 meV with the high scattering angle detector results in the c* || k_i orientation, where one expects no magnetic contributions due to the magnetic form factor, an empirical formula including self-shielding effect and multiple scattering was established to deduce the non-magnetic background for the small angle detectors. This background is then subtracted from the raw data.

In fig. 6 the background corrected spectrum for the incident energy E_i=200meV obtained by the chopper spectrometer MARI at ISIS facility of RAL is displayed. The SW excitation up to 85meV energy transfer can be clearly seen. The inset of fig.6 displays all the SW peak positions along the chain direction observed with different incident energies. The fit with the classical dispersion 4S \[ |J| \sin q \] is shown by the solid line and yields an intrachain exchange J/k_B=-165K. This is to be compared with J/k_B=-117K determined by the bulk susceptibility measurement. A consistent interpretation applying quantum theory for both the bulk susceptibility and SW dispersion measurement as in the case of S=1/2 is highly desirable. Furthermore the observed linewidths can not be explained by the \[ \delta \] function-like SW line shape (see the solid line in fig.6 representing the resolution convoluted classical SW dispersion). A try to apply the SW double continuum as in the case of S=1/2 does not account for the
experimental observations. The detailed line shape analysis indicates that the finite widths observed around $\pi$ can be interpreted as the SW damping at this finite temperature of 40K. But the large linewidths observed around $2\pi$, which cannot be explained by the classical damping, might indicate the $2\pi$-periodic character of the q-dependent linewidths. This resembles the situation observed in S=1/2 and shows that the translation symmetry is not broken.

Figure 7 depicts the full dispersion perpendicular to the chain direction. The overall agreement with the SW prediction is good. Especially the number of the modes predicted by the SW theory are all observed and in contrast to S=1 systems no anomaly in the energy gap around Q=(0,0,1) is observed. One should however note that the mode at 5.3 meV strictly speaking has no cross-section in the conventional SW theory and the mode around 7meV is an out-of-plane mode and therefore should be not visible at (001). A detailed analysis of the spin excitations in other zones shows that the dominant fluctuations are spin fluctuations in the basal plane, i.e. in-plane fluctuations. This suggests that the spin excitation energies in [110]-direction are correctly described by the classical SW theory, but the classical idea of mode assignments to pure in-plane or out-of-plane spin fluctuations does not apply in the S=3/2 system. We mention that in the earlier study the absolute intensities of the low energy acoustic branch towards the Bragg point (1/3,1/3,1) could not be explained by the SW theory either. It should be pointed out, that the deviation in the observed intensities from the classical SW prediction in the S=5/2 system, as reported above, happens to be most pronounced in the same branch.

![Figure 7](image)

The dispersion perpendicular to the chain direction in CsVCl₃. Open points are from ref. [29]. The solid line is a classical SW dispersion with the parameters $J/k_B$=165K, $J'/k_B$=0.52K and $D/k_B$=0.52K.

These results indicate that the quantum effect in the S=3/2 system shows up in the renormalization of the exchange constant, large linewidths around $2\pi$ and probably in the mixing of the spin fluctuation components in the 3-D ordered phase. It is obvious that these consequences of the quantum effect are quite different to those seen in the S=1 system. Hence these detailed neutron scattering results on ABX₃ systems support the original Haldane's claim, in which the different quantum nature of the half-integer and integer spin systems is conjectured.

In summary the detailed and comprehensive neutron scattering studies of spin excitations in ABX₃ systems with different spin values clearly demonstrate the importance of the quantum effect for small S-value systems even in the 3-D ordered phase. In S=1 case the system should be regarded as the ordered Haldane state and the classical SW description totally fails. In S=3/2 system a renormalization of the exchange constant in the chain direction is indicated. The spin excitation energies perpendicular to the chain direction are in reasonable agreement with the SW calculations, but the predicted eigenvectors of the excitations are not consistent with the
experimental findings. In $S=5/2$ system finally, almost a full agreement with the classical SW predictions, both in eigenvalues and eigenvectors of the SW excitations, is found.

Acknowledgement: We have benefited from helpful discussions and collaborations on the experiments described above. In particular we would like to thank I. Affleck, M. Arai, W.J.L. Buyers, B. Dorner, Y. Endoh, K. Hirakawa, H. Kadowaki, J.K. Kjems and R. Pynn. This research was supported in part by the Grant in Aid for the Scientific Research Project of the Japanese Ministry of Education, Science and Culture.

References
CRYSTAL STRUCTURE REFINEMENT OF ALLOYS AND HYDRIDES OF Zr(Mn<sub>1-x</sub>M<sub>x</sub>)<sub>2</sub> WITH M=V, Fe, Co, Ni AND Al

†Etsuo Akiba, †Hiroshi Hayakawa, †Shin Fujitani, †Ikuo Yonezu,
†Daniel Fruchart, †Jean Louis Soubeiryoux, †Liliane Pottinier and †Salbatore Miraglia

National Institute of Materials and Chemical Research
1-1 Higashi, Tsukuba, Ibaraki, 305 Japan

*Sanyo Electric Co Ltd., Functional Materials Research Center
1-18-13 Hashiridani, Hirakata, Osaka, 573 Japan

†Laboratoire de Cristallographie, CNRS
166X, 38042 Grenoble, Cedex 09, France

ABSTRACT

The crystal structures of potential hydrogen absorbing alloys of Zr(Mn<sub>1-x</sub>M<sub>x</sub>)<sub>2</sub> (M=V, Fe, Co, Ni and Al, x=0.2) and their deuterides have been investigated by powder neutron diffraction. The neutron diffraction data were obtained using the D5 diffractometer at the SILOE reactor at the Centre d’Etudes Nucléaires de Grenoble (λ=2.50Å or 1.42Å). The structures of all the alloys are refined to be the C14-type Laves phase (Space group: P6<sub>3</sub>mmm). All the alloys contain the η-carbide type oxide, Zr<sub>3</sub>(Mn<sub>1-x</sub>M<sub>x</sub>)O<sub>2</sub>, in 1-8% as the second phase. All the M atoms randomly occupy two Mn sites (2a and 6h). Deuterium occupied three or four interstitial sites which are composed by two Zr atoms and two Mn/M atoms. Differences in crystal structure with the kinds of M atoms have not been observed.

INTRODUCTION

The Laves phase alloy, ZrMn<sub>2</sub>, is known to absorb a significant amount of hydrogen leading to a hydride with a reasonable hydrogen dissociation pressure. The potential applications of ZrMn<sub>2</sub> are energy conversion, hydrogen purification, hydrogen storage or an electrode material<sup>1</sup>.

Crystal structure of ZrMn<sub>2</sub>D<sub>3</sub> has been refined by Didisheim et al.<sup>2</sup>. ZrMn<sub>2</sub> is a C14-type Laves phase and its hydride is also a C14-type Laves phase which has four tetrahedral interstitial hydrogen sites. However, crystal structure of pseudobinary ZrMn<sub>2</sub> based alloys and their hydrides has not been reported, though pseudobinary LaNi<sub>5</sub> related alloys have been intensively investigated<sup>3</sup>.

In order to control the dissociation pressure for the alloy-hydrogen systems, substitution of the metal to the binary system has been widely carried out. This method has also been used for modification of the properties of hydrogen absorbing alloys such as flatness of the plateau and decrease in the width of hysteresis. Some of the authors<sup>1</sup> have studied the effect of substitution of M=V, Fe, Co, Ni in the system Zr(Mn<sub>1-x</sub>M<sub>x</sub>)<sub>2</sub> by X-ray diffraction measurements, equilibrium hydrogen pressure determinations and calculations using the Miedema’s model<sup>4</sup><sup>,</sup><sup>5</sup>. They have found the linear relationship between hydrogen equilibrium
pressure and the cell volume for the alloy in which the metals except nickel are substituted\(^1\). The alloys modified by nickel show the opposite tendency to other alloys.

The positions of M metals in the unit cell can not be refined using X-ray diffraction data because atomic numbers of M atoms and Mn are close. Therefore, in the previous work the opposite tendency of the Zr\((\text{Mn}_{1-x}\text{Ni}_x)\) system can not be understood from the structural viewpoint.

In this work, in order to determine the sites for hydrogen occupation and substitution of M metals in the Zr\((\text{Mn}_{1-x}\text{M}_x)\) alloys we have used powder neutron diffraction technique. There is a high contrast between the neutron scattering lengths of the manganese atoms and that of the M metals. Therefore, the site occupation of these metals can be distinguished. Hydrides of these alloys have been prepared to the highest hydrogen content making them stable under normal conditions. The location of the D atoms in the interstitial sites of Zr\((\text{Mn}_{1-x}\text{M}_x)\)\(_2\)\(\text{D}_y\) structures have also been studied by powder neutron diffraction.

**EXPERIMENTAL**

The Zr\((\text{Mn}_{1-x}\text{M}_x)\) alloys \((\text{M} = \text{V, Fe, Co, Ni, Al})\) with \(x = 0.2\) have been prepared by the arc melting method from 99.9% pure metals in a high purity argon atmosphere. The composition of the prepared Zr\((\text{Mn}_{1-x}\text{M}_x)\) alloys was checked by chemical analysis and the results are listed in Table 1. In the previous study\(^1\), the alloys were not annealed. For this study the alloys were annealed at 1273K for 28.8 ks. The weight loss by annealing was less than 0.4%. The alloys were crushed in a glove-box under a 99.99% purity argon gas atmosphere to prevent combustion. Half of each sample batch was then hydrogenated (deuterated for neutron diffraction) changing temperature between room temperature and 523K and at pressures ranging from 3 to 5 MPa in designed stainless steel autoclaves. The deuterium uptake by the alloys was determined by a gravimetric method. All the samples were checked by standard X-ray analysis\((\lambda_{\text{CuK}α})\) using a Philips diffractometer equipped with a back scattering graphite monochromator.

The neutron diffraction experiments were carried out using the DN5 diffractometer at the SILOE reactor at the Centre d'Etudes Nucléaires de Grenoble which is equipped with a position sensitive detector of 800 cells covering 80 degree in the \(2θ\) range. Two wavelengths were mainly used: 2.50\(Å\) or 1.42\(Å\) from a graphite monochromator. The hydride patterns have been recorded at low temperature\((30K)\) using a helium flow cryostat to determine the hydrogen atom positions more accurately. The diffraction patterns were analyzed using profile refinement software package "FULLPROF"\(^6\).

**RESULTS**

Structural parameters for Zr\((\text{Mn}_{1-x}\text{M}_x)\) alloys

Fig. 1 shows the results of Rietveld analysis using powder neutron diffraction data measured at room temperature for the alloy of Zr\(\text{Mn}_{1.6}\text{V}_{0.4}\) (\(λ = 2.50\text{Å}\)). The structures of all the alloys were refined and were found to be the C14 structure \((\text{space group}; P6_3/mmc)\). The second phase identified as being the cubic suboxide of \(η\)-carbide type of structure Zr\(3(\text{Mn}_{1-x}\text{M}_x)\)\(3\text{O}\)) is more or less present in all the alloys \((\text{these compounds in the } Fd3m\text{ space group have been considered in the multiphase refinement})\). The short bars of the second row under the profile in Fig. 1 are shown the positions of diffractions by the Zr\(3(\text{Mn}_{1-x}\text{V}_x)\)\(3\text{O}\). These refinements have been carried out under following assumptions; Mn/M metals fully occupy the 2\(a\) and 6\(h\) sites and Mn and M atoms are randomly distributed to the sites. However,
Fig. 1 The results of Rietveld analysis for ZrMn$_{1.6}$V$_{0.4}$ at 295K.

Observation: dots, Calculated profile: line,
Upper vertical bars: C14 Laves phase, Lower vertical bars: Zr$_3$(Mn$_{1-x}$V$_x$)$_3$O phase

<table>
<thead>
<tr>
<th>Alloys</th>
<th>AI</th>
<th>V</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrMn$<em>{1.6}$M$</em>{0.4}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a(Å)</td>
<td>5.1102(2)</td>
<td>5.0614(4)</td>
<td>5.025(3)</td>
<td>5.0063(3)</td>
<td>5.0161(5)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>8.3426(5)</td>
<td>8.3075(7)</td>
<td>8.2472(5)</td>
<td>8.2058(6)</td>
<td>8.2138(9)</td>
</tr>
<tr>
<td>Zr 4f(1/3,2/3,z)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>z</td>
<td>0.4386(3)</td>
<td>0.4335(4)</td>
<td>0.4376(3)</td>
<td>0.4372(3)</td>
<td>0.4392(5)</td>
</tr>
<tr>
<td>Mn/M 2a : (0,0,0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m$_{Mn}$</td>
<td>0.411(3)</td>
<td>0.423(3)</td>
<td>0.423(3)</td>
<td>0.381(3)</td>
<td>0.441(3)</td>
</tr>
<tr>
<td>n$<em>{M}$ = (0.5 - m$</em>{Mn}$)</td>
<td>0.090(3)</td>
<td>0.078(3)</td>
<td>0.078(3)</td>
<td>0.117(3)</td>
<td>0.060(3)</td>
</tr>
<tr>
<td>Mn/M</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6h(2x,1/4)</td>
<td>0.835(1)</td>
<td>0.826(1)</td>
<td>0.830(2)</td>
<td>0.825(1)</td>
<td>0.831(4)</td>
</tr>
<tr>
<td>m$_{Mn}$</td>
<td>1.206(6)</td>
<td>1.179(3)</td>
<td>1.212(3)</td>
<td>1.140(6)</td>
<td>1.218(3)</td>
</tr>
<tr>
<td>m$<em>{M}$ = (1.5 - m$</em>{Mn}$)</td>
<td>0.294(6)</td>
<td>0.321(3)</td>
<td>0.288(3)</td>
<td>0.360(6)</td>
<td>0.282(3)</td>
</tr>
<tr>
<td>Proportion of</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr$<em>3$(Mn$</em>{1-x}$M$_x$)$_3$O</td>
<td>4%</td>
<td>8%</td>
<td>4%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>a(Å) of</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr$<em>3$(Mn$</em>{1-x}$M$_x$)$_3$O</td>
<td>11.947(2)</td>
<td>11.932(2)</td>
<td>11.856(3)</td>
<td>11.913(5)</td>
<td>11.847(8)</td>
</tr>
<tr>
<td>Rp %</td>
<td>3.4</td>
<td>3.9</td>
<td>2.6</td>
<td>2.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Rp %</td>
<td>3.7</td>
<td>6.8</td>
<td>6.7</td>
<td>4.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Composition (neutron)</td>
<td>ZrMn$<em>{1.65}$Al$</em>{0.35}$</td>
<td>ZrMn$<em>{1.60}$V$</em>{0.40}$</td>
<td>ZrMn$<em>{1.60}$Fe$</em>{0.40}$</td>
<td>ZrMn$<em>{1.57}$Co$</em>{0.43}$</td>
<td>ZrMn$<em>{1.60}$Ni$</em>{0.40}$</td>
</tr>
<tr>
<td>Composition (chemical analysis)</td>
<td>ZrMn$<em>{1.60}$Al$</em>{0.40}$</td>
<td>ZrMn$<em>{1.58}$V$</em>{0.40}$</td>
<td>ZrMn$<em>{1.60}$Fe$</em>{0.42}$</td>
<td>ZrMn$<em>{1.60}$Co$</em>{0.40}$</td>
<td>ZrMn$<em>{1.81}$Ni$</em>{0.43}$</td>
</tr>
</tbody>
</table>
occupation parameters of each element, \( \eta_{(2d)} \) and \( m_{(6h)} \), were refined. The formulas obtained by neutron and the chemical analyses are listed in Table 1 with the other structural parameters.

Structural parameters for Zr(Mn\textsubscript{1-x}M\textsubscript{x})\textsubscript{2}D\textsubscript{y} samples

The structural refinements have been carried out on data recorded at 30K with \( \lambda = 1.42 \) Å. Fig. 2 shows the results from Rietveld analysis for diffraction data of ZrMn\textsubscript{1.6}V\textsubscript{0.4}D\textsubscript{3.5} measured at 30K. The hydrides ZrMn\textsubscript{1.6}V\textsubscript{0.4}D\textsubscript{3.5}, ZrMn\textsubscript{1.6}Co\textsubscript{0.4}D\textsubscript{3.0} and ZrMn\textsubscript{1.6}Ni\textsubscript{0.4}D\textsubscript{3.0} retain the C14 structure as the main phase. The hydride ZrMn\textsubscript{1.6}Al\textsubscript{0.4}D\textsubscript{2.5} is found to be not fully hydrogenated and the sample contains two C14-type structures such as the deuteride and the starting alloy, and the \( \eta \)-carbide type oxide. The hydride, ZrMn\textsubscript{1.6}Fe\textsubscript{0.4}D\textsubscript{3.0}, shows the C14 structure with extra lines at \( d = 7.85 \) Å and 5.09 Å. These extra lines disappeared above 150K and are attributed to a magnetic origin. These magnetic lines are also found in all the alloys investigated at low temperature.

We found that the suboxide phase was also hydrogenated to form Zr\textsubscript{3}(Mn\textsubscript{1-x}M\textsubscript{x})\textsubscript{3}O\textsubscript{y} type hydride as reported by Rotella et al.\textsuperscript{7).} The hydrided suboxides have a large cubic cell of 12.4-12.5 Å.

Table 2 lists the results obtained in the final refinements for ZrMn\textsubscript{1.6}M\textsubscript{0.4}D\textsubscript{y}. The diffraction patterns of the deuteride compounds exhibited a wavy background. This modulation involves a distance about 2.1 Å that is roughly the H-H minimum distance of simultaneously occupied interstitial sites\textsuperscript{8).} Therefore, the shape of the background is influenced by the state or behavior of deuterides in the alloys.

Fig. 2 The results of Rietveld analysis for ZrMn\textsubscript{1.6}M\textsubscript{0.4}D\textsubscript{y} at 30K.
In the deuterated samples, we have not assumed the rearrangement of the substituted M atoms on the two metal sites 2α and 6h, we have used the ones previously determined on the alloys. However we have refined the atomic parameters of the metals that can change with hydrogenation. The deuterium atoms are located in the Zr₂(Mn/M)(A₂B₂) tetrahedral sites of the C14 structure. The four deuterium sites of A₂B₂ type (D1, D2, D3 and D4) have been assumed in the refinements with free occupational parameters. The formula obtained are listed in Table 2 and for comparison those determined by the gravimetric method are also listed.

**Table 2** Structural parameters of ZrMn₁.₆M₀.₄Dy at 30K

<table>
<thead>
<tr>
<th>Deuterides</th>
<th>ZrMn₁.₆M₀.₄Dy</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>5.399(1)</td>
<td>5.4614(5)</td>
<td>5.3934(9)</td>
<td>5.3916(7)</td>
<td>5.371(3)</td>
<td></td>
</tr>
<tr>
<td>c(Å)</td>
<td>8.828(2)</td>
<td>8.8953(9)</td>
<td>8.791(2)</td>
<td>8.780(1)</td>
<td>8.729(5)</td>
<td></td>
</tr>
<tr>
<td>Zr 4f: (1/3,2/3,x)</td>
<td>0.437(1)</td>
<td>0.435(8)</td>
<td>0.4345(9)</td>
<td>0.4320(9)</td>
<td>0.442(3)</td>
<td></td>
</tr>
<tr>
<td>Mn/M 2α: (0,0,0)</td>
<td>0.411</td>
<td>0.423</td>
<td>0.423</td>
<td>0.381</td>
<td>0.441</td>
<td></td>
</tr>
<tr>
<td>mM = (0.5 - mM)</td>
<td>0.090</td>
<td>0.078</td>
<td>0.078</td>
<td>0.117</td>
<td>0.060</td>
<td></td>
</tr>
<tr>
<td>Mn/M 6h: (x,2x,1/4)</td>
<td>0.847(5)</td>
<td>0.826(1)</td>
<td>0.835(5)</td>
<td>0.833(3)</td>
<td>0.827(4)</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>1.206</td>
<td>1.179</td>
<td>1.121</td>
<td>1.140</td>
<td>1.218</td>
<td></td>
</tr>
<tr>
<td>mM</td>
<td>0.294</td>
<td>0.321</td>
<td>0.288</td>
<td>0.360</td>
<td>0.282</td>
<td></td>
</tr>
<tr>
<td>D1 24l: (x,y,z)</td>
<td>0.051(3)</td>
<td>0.051(2)</td>
<td>0.042(2)</td>
<td>0.046(2)</td>
<td>0.057(6)</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.340(3)</td>
<td>0.339(2)</td>
<td>0.323(2)</td>
<td>0.330(2)</td>
<td>0.341(6)</td>
<td></td>
</tr>
<tr>
<td>y</td>
<td>0.577(2)</td>
<td>0.561(1)</td>
<td>0.566(2)</td>
<td>0.560(1)</td>
<td>0.572(5)</td>
<td></td>
</tr>
<tr>
<td>z</td>
<td>1.47(4)</td>
<td>1.41(3)</td>
<td>1.22(3)</td>
<td>1.30(3)</td>
<td>1.24(4)</td>
<td></td>
</tr>
<tr>
<td>D2 12k: (x,2x,z)</td>
<td>0.467</td>
<td>0.448(2)</td>
<td>0.460(3)</td>
<td>0.451(3)</td>
<td>0.460(8)</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
<td></td>
</tr>
<tr>
<td>y</td>
<td>0.50(4)</td>
<td>1.27(2)</td>
<td>1.09(2)</td>
<td>1.20(3)</td>
<td>1.05(8)</td>
<td></td>
</tr>
<tr>
<td>D3 6h: (x,2x,1/4)</td>
<td>0.447(5)</td>
<td>0.442(3)</td>
<td>0.463(3)</td>
<td>0.456(3)</td>
<td>0.452(9)</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.48(2)</td>
<td>0.48(1)</td>
<td>0.60(1)</td>
<td>0.67(1)</td>
<td>0.62(2)</td>
<td></td>
</tr>
<tr>
<td>y</td>
<td>0.196</td>
<td>0.190(4)</td>
<td>0.198</td>
<td>0.198</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>D4 6h: (x,2x,1/4)</td>
<td>0.11</td>
<td>0.26(1)</td>
<td>0.11</td>
<td>0.03</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

**Proportion of Zr₃(Mn₁₋ₓMₓ)ₙO**

<table>
<thead>
<tr>
<th>Zr₃(Mn₁₋ₓMₓ)ₙO</th>
<th>4%</th>
<th>8%</th>
<th>1%</th>
<th>1%</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å) of Zr₂(Mn₁₋ₓMₓ)ₙO</td>
<td>12.529(6)</td>
<td>12.352(4)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rp %</td>
<td>3.4</td>
<td>3.9</td>
<td>2.6</td>
<td>2.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Rg %</td>
<td>3.7</td>
<td>6.8</td>
<td>6.7</td>
<td>4.2</td>
<td>8.9</td>
</tr>
<tr>
<td>y (neutron)</td>
<td>2.60</td>
<td>3.45</td>
<td>2.91</td>
<td>3.10</td>
<td>2.91</td>
</tr>
<tr>
<td>y (gravimetric)</td>
<td>2.60</td>
<td>3.49</td>
<td>2.90</td>
<td>3.01</td>
<td>2.96</td>
</tr>
<tr>
<td>ΔV/H in unit cell (Å³)</td>
<td>13.1</td>
<td>13.2</td>
<td>13.6</td>
<td>13.8</td>
<td>13.4</td>
</tr>
</tbody>
</table>
DISCUSSION

Zr(Mn_{1-x}M_x)_2 alloys

The lattice parameter variation with substitution to the Mn sites is obtained as follows:

\[ \text{ZrMn}_{1.6}\text{Co}_{0.4} < \text{ZrMn}_{1.6}\text{Ni}_{0.4} < \text{ZrMn}_{1.6}\text{Fe}_{0.4} < \text{ZrMn}_2 < \text{ZrMn}_{1.6}\text{V}_{0.4} < \text{ZrMn}_{1.6}\text{Al}_{0.4} \]

The lattice parameters of ZrMn2 are \( a = 5.026\,\text{Å} \) and \( c = 8.250\,\text{Å} \) as reported by Nishimiya\(^9\). This order agrees with the previous results\(^1\) on the as-cast alloys. The variation of the z parameters for the zirconium site does not follow the atom size sequence and seems to be more correlated to the substitutions of the M atoms to the 2a and 6h sites. The occupation of substituted metals in the 2a site is in the sequence of Ni<Fe<Al<V and that in the 6h site is that of Ni<Fe<Al<V<Co.

Zr(Mn_{1-x}M_x)_2D_y deuterides

The deuterium sites in the C14 structure are the tetrahedral sites formed by two zirconium atoms and two Mn or M atoms (A2B2). The D4 site is only significantly occupied in the vanadium substituted alloy, because vanadium is an only hydride forming metal among substituted metals. On the other hand, the occupation in the D2 site for ZrMn_{1.6}Al_{0.4}D_y is less than others. It reflects that the Al substituted alloy has the lowest hydrogen capacity among the alloys investigated. The occupancies in the D1 and D3 sites are almost the same in all the deuterides.

The relative cell volume expansion (the alloy to the hydride) is shown in Table 2. This value gives an estimation of the hydrogen-induced volume increase. Since four chemical formulae in a unit cell, hydrogen induced volume increase from the alloys to the deuterides per D atom is 3.3-3.5\,\text{Å}^3, which are close to the reported value 2.3\,\text{Å}^3/H\(^{10}\).

Crystal structural data indicate that all the substituted alloys and hydrides behave in the same manner. Therefore, we cannot explain the presence of a double plateau in the pressure composition isotherm and unusual relationship between the lattice volume and hydrogen equilibrium pressure of the alloys modified by nickel\(^1\). In the previous report\(^1\) the content of nickel in the Zr(Mn_{1-x}Ni_x)_2 samples is x=0.05 and 0.1 but x=0.2 for this work. Suzuki and Nishimiya\(^1\) reported that hydrogen equilibrium pressure and the lattice volume for the alloy of x=0.5. The relation between the cell volume and hydrogen equilibrium pressure is different in the alloys with the lower nickel content to those with the higher one. This suggests that behaviors of Zr(Mn_{1-x}Ni_x)_2 may depend upon the content of nickel. Detailed measurements on crystal structure and equilibrium pressure are needed for understanding the behaviors of Zr(Mn_{1-x}Ni_x)_2.

CONCLUSIONS

This neutron diffraction study on pseudobinary alloys Zr(Mn_{1-x}M_x)_2 with M=V, Fe, Co, Ni and Al; x=0.2 and the corresponding hydrides has given the following results:

1 - All the M metal atoms of Zr(Mn_{1-x}M_x)_2 randomly occupy the manganese sites (the 2a and 6h sites) of the C14 structure (Space group: \text{P6}_3\text{mm}c).

2 - The second phase of the \( \eta \)-type oxide, Zr_{3}(Mn_{1-x}M_x)\text{3}O, has been observed and the content of this phase is the largest in the vanadium substituted compound. On hydrogenation, the hydride of this second phase is formed.
3. There are four hydrogen sites (D1-D4) with tetrahedral symmetry in the C14 structure. All the sites consist of two zirconium atoms and two manganese/M atoms. Hydrogen (deuterium) is mainly located in the D1 and D2 sites. However, the occupations in these sites differ with the kinds of M metals.

4. Hydrogen induced volume increase from the alloys to the deuterides per D atom is 3.3-3.5Å³. The hydrogen expansion rule postulated by Westlake is fulfilled for this series of compounds.

REFERENCES

6. FULLPROF: Software package written by J. Rodriguez-Carvajal of Institute Laue Langevin, modified version of DBW by R. A. Young of Georgia Institute of Technology.
NEUTRON DEPOLARIZATION STUDIES
ON MAGNETIC FLUX IN SUPERCONDUCTORS

T. WATANABE(1), S. ITOH(2), K. YAMADA(1), H. KOJIMA(3),
I. TANAKA(3), N. TOYOTA(4), Y. ENDOH(1)

(1) Department of Physics, Tohoku University, Aramaki, Sendai 980, Japan
(2) National Laboratory for High Energy Physics, Tsukuba, Ibaragi 311, Japan
(3) Institute of Inorganic Synthesis, Yamanashi University, Kofu 400, Japan
(4) Institute for Materials Research, Katahira, Aoba-ku, Sendai 980, Japan

Neutron depolarization measurements were performed on the magnetic flux state trapped in the superconducting single crystals by using TOP polarized neutron spectrometer installed at the pulsed neutron facility at the National Laboratory for High Energy Physics (KEK).

Neutron depolarization of the wavelength dependence senses the magnetic induction of mesoscopic scale inside the bulk material. The polarization of transmitted neutron beams is related to the Larmor precession of neutron polarization vector around the pinned magnetic fluxes in superconductor.

We have measured high temperature oxide superconductor single crystalline plate \( \text{La}_{1.86}\text{Sr}_{0.15}\text{CuO}_4 \) (\( T_c = 36 \text{K} \)) were grown by the Traveling-Solvent-Floating-Zone method and A15 typical type-II superconductor \( \text{V}_3\text{Si} \) (\( T_c = 16.1 \text{K} \)) single crystal were grown by the Electron-Beam-Floating-Zone method. We can detect the magnetic flux sensitively by the wavelength dependence of polarization at varying temperature and applied magnetic field. In these measurements the lower critical fields are readily determined from the zero field cooling process. We can see the strong C-axis anisotropy of \( \text{H}_1 \) of \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \) single crystal. The damping oscillations in polarization with respect to neutron wavelength represent the spatial distribution of the magnetic flux in the crystal. We can determine the magnetic penetration depth from the damping factor in field cooling process measurements. The temperature dependence of the penetration depth of \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \) and \( \text{V}_3\text{Si} \) is interpreted by the BCS theory.
MAGNETIC STRUCTURE IN SINGLE CRYSTAL OF ANTFERROMAGNETIC HEAVY FERMIION SUPERCONDUCTOR UPd$_2$Al$_3$

H. KITA, A. DÖNNI, Y. ENDOH, K. KAKURAI$^\dagger$, N. SATO and T. KOMATSUBARA

Department of Physics, Tohoku University, Aramaki, Aoba-ku, Sendai 980, Japan

$^\dagger$Institute for Solid State Physics, Tokyo University, Roppongi, Minato-ku, Tokyo 106, Japan

ABSTRACT

The magnetic phase diagram of UPd$_2$Al$_3$ has been determined up to 5 Tesla by single crystal neutron scattering experiments performed above and below the superconducting transition at $T_c = 2$ K. At non-zero field the observed magnetic intensities correspond to the zero-field propagation vector $\mathbf{k} = [0, 0, 1/2]$. From the observed field induced changes of magnetic peak intensities we conclude that at zero field the ordered uranium moments point along hexagonal a directions. A magnetic field applied inside the easy a-b plane gives rise to domain reorientations and in addition rotates the direction of the ordered moments against a small anisotropy inside the a-b plane to become perpendicular to the field direction.

INTRODUCTION

The heavy-fermion superconductor UPd$_2$Al$_3$ discovered by Geibel et al. [1] crystallizes in the hexagonal PrNi$_2$Al$_3$ structure (space group P6/mmm). Bulk measurements revealed antiferromagnetic ordering below $T_N = 14$ K and a transition to a superconducting ground-state at $T_c = 2$ K. The kind of antiferromagnetic structure of UPd$_2$Al$_3$ was determined in a powder neutron diffraction experiment [2]. Ferromagnetic sheets with the ordered magnetic moments of uranium lying in the easy a-b plane are coupled antiferromagnetically along the c axis. This magnetic order corresponds to a doubling of the chemical unit cell with an ordering vector $\mathbf{k} = [0, 0, 1/2]$. The ordered magnetic uranium moment of $\mu_U = 0.85(3) \mu_B$ at saturation coexists with the superconducting state. This is by far the largest $\mu_U$ value observed for any heavy fermion superconductor so far. The direction of the ordered moments inside the a-b plane could not be determined in the powder neutron diffraction experiment.
Single crystal magnetic measurements (dc susceptibility, dc magnetization, magneto-resistivity and magnetoresistance) have established [3] a richly varied magnetic phase diagram in UPd$_2$Al$_3$ with three phases for magnetic fields in the easy a-b plane but only one for fields along the magnetically hard c axis.

We used a large UPd$_2$Al$_3$ single crystal of 450 mm$^3$ volume and performed elastic neutron scattering experiments in external magnetic fields up to 5 Tesla. In this paper we present the determination of the kind of magnetic field induced structures in UPd$_2$Al$_3$ measured both above and below the superconducting transition at 4.5 K and at 0.4 K, respectively.

EXPERIMENTAL

Our UPd$_2$Al$_3$ single crystal with $T_N = 14.3$ K and $T_c = 1.8$ K was prepared by the Czochalsky pulling method [4]. Elastic neutron scattering experiments were performed on the triple-axis spectrometer TOPAN at the JRR3M reactor at JAERI, Tokai, Japan, by using neutron wavelengths of 2.44 Å and 1.64 Å. An external magnetic field was applied vertical to the scattering plane by means of a superconducting He4 magnet reaching 2 Tesla and by using an Oxford dilution cryostat with a 5 Tesla magnet. Two different sample orientations were chosen with the hexagonal (h, h, l) reflections and the (h, 0, l) reflections in the horizontal scattering plane. The resulting directions of the external magnetic field are in the easy a-b plane perpendicular and parallel to the a direction, respectively.

RESULTS AND DISCUSSION

Above the superconducting phase transition at 4.5 K at saturation the zero field magnetic intensities observed at the 14 inequivalent reflections (0, 0, 1/2), (0, 0, 3/2), (0, 0, 5/2), (0, 0, 7/2), (1, 0, 1/2), (1, 0, 3/2), (1, 0, 5/2), (1, 1, 1/2), (1, 1, 3/2), (2, 0, 1/2), (2, 0, 3/2), (2, 2, 1/2), (2, 2, 3/2) and (3, 0, 1/2) confirm the reported antiferromagnetic structure of UPd$_2$Al$_3$ [2] with the magnetic propagation vector being $\mathbf{k} = [0, 0, 1/2]$ and the ordered uranium moments lying in the a-b plane. At the measured nonzero fields magnetic intensity is observed at above reflections and at no additional reflections which shows that also the nonzero-field structures of UPd$_2$Al$_3$ correspond to the zero field propagation vector $\mathbf{k} = [0, 0, 1/2]$. For both measured field directions the intensities of the magnetic reflections (0, 0, k/2), k= 1, 3, 5, 7 are observed to be field independent. Thus the antiferromagnetically ordered uranium moments are in the a-b plane and there is no field induced component out of this plane.

Fig. 1 shows the field dependence of the magnetic (0, 0, 1/2) and (1, 1, 1/2) reflections measured at 4.5 K in a magnetic field perpendicular to the hexagonal a and c directions. The (0, 0, 1/2) peak is field independent. The intensity of the (1, 1, 1/2) reflection strongly decreases down to 17% of the zero field value at 1.2 T and is constant at higher fields. The pronounced hysteresis behavior below 1.2 T is typical for a domain reorientation process of an antiferromagnet.

Fig. 2 shows the field dependence of the magnetic (0, 0, 3/2) and (1, 0, 1/2) reflections
**Fig. 1:** Field dependence of the magnetic (0, 0, 1/2) and (1, 1, 1/2) reflections measured at 4.5 K in a magnetic field perpendicular to the hexagonal a and c directions. Solid lines correspond to the calculated high field intensities of 1.0 and 0.169 for the peaks (0, 0, 1/2) and (1, 1, 1/2), respectively.

**Fig. 2:** Field dependence of the magnetic (0, 0, 3/2) and (1, 0, 1/2) reflections measured at 4.5 K in a magnetic field parallel to the hexagonal a direction. Solid lines correspond to the calculated high field intensities of 1.0 and 0.381 for the peaks (0, 0, 3/2) and (1, 0, 1/2), respectively.
measured at 4.5 K in a magnetic field parallel to the hexagonal a direction. The (0, 0, 3/2) peak is field independent. The intensity of the (1, 0, 1/2) reflection decreases by showing hysteresis behavior for $H \leq 0.9$ T. At higher fields there is a further approximately linear decrease without hysteresis from 60% of the zero field value at 0.9 T down to 37% at 4.3 T. Above 4.3 T the intensity is constant.

The observed field dependence of the magnetic intensities of UPd$_2$Al$_3$ can be reproduced by the following model. Compared to the magnetically hard c direction the anisotropy in the easy a-b plane is small. At zero field the antiferromagnetically ordered uranium moments point along a directions. The hexagonal crystal symmetry of UPd$_2$Al$_3$ gives rise to three magnetic domains with different spin directions. In an antiferromagnet an external magnetic field favors the magnetic domains which are the most perpendicular to the field direction.

An external field applied inside the a-b plane destroys the energetically unfavored domains and in addition rotates the direction of the ordered moments against the small anisotropy inside the easy a-b plane to become perpendicular to the field direction. In an external field along the c axis the field equally favors all three magnetic domains which are perpendicular to the field and the zero field structure of UPd$_2$Al$_3$ is maintained as confirmed by the magnetic measurements [3].

In an external field being perpendicular to both a and c axis the experimentally observed results (Fig. 1) are explained by the model as shown in Fig. 3. In the state I' the observed hysteresis behavior of the (1, 1, 1/2) peak (see Fig. 1) corresponds to a domain reorientation process. At $H_{c1} = 1.2(1)$ T the magnetic field has fully destroyed the two energetically unfavored domains. The state II' is a one domain state. Since the ordered moments of this domain are perpendicular to the field direction the observed intensities are constant and within experimental error agree well with the calculated values (solid lines in Fig. 1).

In an external magnetic field parallel to the a axis the experimentally observed results (Fig. 2) are explained by the model as shown in Fig. 4. The destroying of the energetically unfavored domain with the ordered moments parallel to the field direction gives rise to a the observed hysteresis behavior for $H < H_{c1}$. The ordered moments of the other two domains are rotated away from the a direction to become perpendicular to the direction of the external field. In state I both processes are superposed and in state II the latter process gives rise to the observed approximately linear decrease of the (1, 0, 1/2) intensity in Fig. 2 towards the calculated value at $H_{c2} = 4.3(2)$ T. Above $H_{c2}$ a one domain state with the ordered moments perpendicular to the field direction is realized and the observed intensities are constant (Fig. 2).

At 5 Tesla and 4.2 K the magnetization of UPd$_2$Al$_3$ for fields perpendicular to the c axis gives rise to a magnetic field induced ferromagnetic component of 0.11(1) $\mu_B$ [4] which is much smaller than the size of the ordered zero-field antiferromagnetic moment of 0.85(3) $\mu_B$ [2]. Within experimental error the latter value is constant in magnetic fields up to 5 Tesla (see Figs. 1 and 2). The anisotropy in the easy a-b plane reflected by the small difference between $H_{c1} = 0.9(1)$ T and $H_{c1} = 1.2(1)$ T at 4.5 K could not be observed in the magnetization measurement [4]. Between the different states of UPd$_2$Al$_3$ (I' and II' in Fig. 3; I, II and III in Fig. 4) there are no magnetic phase transitions. The magnetic phase diagram of UPd$_2$Al$_3$ up to 5 Tesla shows a normal behavior of an antiferromagnet with domain reorientations and rotations of the antiferromagnetically ordered moments.
Fig. 3: The effect of a magnetic field applied perpendicular to the hexagonal a and c axis on the magnetic structure of UPd$_2$Al$_3$ described by the model. The hexagons correspond to Wigner-Seitz cells in the direct space. At zero field the ordered uranium moments indicated by arrows point along a directions.

Fig. 4: The effect of a magnetic field applied parallel to the hexagonal a axis on the magnetic structure of UPd$_2$Al$_3$ described by the model. The hexagons correspond to Wigner-Seitz cells in the direct space. At zero field the ordered uranium moments indicated by arrows point along a directions.
By cooling our UPd$_2$Al$_3$ crystal from 4.5 K down to 0.4 K the magnetic peak intensities of the (0, 0, 3/2) and (1, 0, 1/2) reflections show no anomaly around the superconducting transition at $T_c = 1.8$ K. The saturated antiferromagnetic structure of UPd$_2$Al$_3$ coexists with the superconducting state. At 0.4 K the measured field dependence of the (0, 0, 3/2) and (1, 0, 1/2) reflections looks similar to Fig. 2 with slightly larger values for $H_{c1} = 1.0(1)$ T and $H_{c2} = 4.7(2)$ T at 0.4 K compared to 4.5 K.

ACKNOWLEDGMENTS

Financial support from the Japan Society for the Promotion of Science is gratefully acknowledged.

REFERENCES


NEUTRON SCATTERING STUDY OF UX₂ (X=Ga,Ge)

Yutaka KUROIWA, Masahumi KOHGI, Toyotaka OSAKABE, Noriaki SATO
and *Yoshichika ŌNUKI

Department of physics, Faculty of science, Tohoku University
Aramaki Aoba, Aoba-ku, Sendai 980, Japan

*Institute of Materials Science, University of Tsukuba
Tennoudai 1-1-1, Tsukuba 305, Japan

ABSTRACT

Neutron scattering experiments were performed on UGa₂ and UGe₂. For UGa₂, spin wave excitations were observed. The excitation energy is nearly constant with the value of about 8 meV in the (0,0,1) plane and shows the dispersion of about 4 meV along [0,0,1] direction. No clear crystal field excitation was detected for both compounds for energy transfer below 500 meV (UGa₂) and 200 meV (UGe₂).

INTRODUCTION

UGe₂ is a ferromagnetic material which has orthorhombic ZrSi₂-structure with lattice constants of a=4.09 Å, b=15.20 Å and c=3.96 Å. Its Curie temperature is 52 K and saturation moment is 1.4 μₜ. The easy axis is the c-axis. Along a- and b-axis, however, the magnetization is below about 0.1 μₜ even at 8 tesla. This material has rather large electronic specific heat coefficient of 35 mJ/mol/K² and shows a heavy cyclotron mass of 25 m₀. These heavy electron like properties indicate that the 5f electron in UGe₂ is itinerant or that the hybridization effect is strong. On the other hand, UGa₂ is also anisotropic ferromagnet with hexagonal AlB₂-structure with lattice constants of a=4.21 Å and c=4.02 Å. Its Curie temperature is 125 K and saturation moment is 2.7 μₜ. The easy axis is the a-axis, and the c-axis is the difficult magnetization direction. The value of saturation moment is close to that of a free ion of U³⁺ or U⁴⁺, and XPS spectra indicate that the f-d hybridization in UGa₂ is small. Thus UGa₂ is regarded as a good reference material to study the heavy electron anomalies in UGe₂. We performed neutron scattering experiments in order to investigate the 5f electronic states in these materials.
EXPERIMENTAL DETAILS

The neutron scattering experiments were performed on the chopper spectrometer INC at the spallation neutron source KENS in National Laboratory for High Energy Physics and the triple axis spectrometer TOPAN at JRR-3M reactor in Japan Atomic Energy Research Institute. The polycrystalline samples of 23.7 g (UGa₂) and 37.3 g (UGe₂) and single crystalline samples of 3.1 g (UGa₂) and 3.0 g (UGe₂) were used. The size of each single crystalline sample is 2-3 mm in diameter and about 30 mm in length.

RESULTS AND DISCUSSION

We performed the inelastic scattering experiments on the polycrystalline samples of UGa₂ and UGe₂ at the INC spectrometer for the energy transfer below 500 meV (UGa₂) and 200 meV (UGe₂). Fig. 1 shows the spectra of UGa₂ and UGe₂ at about 20 K, 100 K (UGe₂) and 200 K (UGa₂) at the scattering angles from 5 to 12 degrees with incident neutron energy of 60 meV. Dashed lines show the phonon contribution estimated from high angle (about 130 degrees) scattering data. For UGa₂, magnetic excitations are seen for energy transfer below about 10 meV. From the spectral shape and temperature dependence, the scattering can be ascribed to the spin wave excitations. For UGe₂, however, no well defined excitation is seen in the spectra. No other well defined magnetic excitation was detected for both compounds in the polycrystalline experiments for energy transfer below 200 meV (UGe₂) and 500 meV (UGa₂) within the experimental error of the peak cross section of about 2 mbarn/sr/Uranium atom.

---

Fig. 1 Inelastic scattering spectrum of UGa₂ and UGe₂ measured on the INC spectrometer.
In order to determine the spin wave dispersion relation of UGa₂, we measured the excitations using the single crystalline sample of UGa₂ on the TOPAN spectrometer with fixed incident neutron energy of 30 meV and fixed scattered neutron energy of 13.7 meV. Here, we show the spectra of the typical constant-Q scans at about 10K in Fig. 2. The horizontal bars shown in the figures indicate the resolution width (FWHM). Well defined magnetic excitations are seen in the figure. The solid lines show the best fit to the data using two Gaussians as the spectral function for the resolution broadened spin wave excitation and the incoherent elastic scattering. Fig. 3 shows the temperature dependence of the excitations at Q=(1.2,0,0). The obtained dispersion relation of the spin wave excitations at about 10K is shown in Fig. 4.

We also tried to observe the spin wave scattering from the single crystalline sample of UGe₂ at the TOPAN spectrometer. However, no clear magnetic scattering could be detected.

Fig. 2 Typical constant-Q scans in UGa₂ at about 10K.

Fig. 3 Temperature dependence of the excitations at Q=(1.2,0,0) in UGa₂.
It is quite interesting that no clear crystal field excitation was observed for both compounds. It may be thought that the peaks of the crystal field excitations are broadened and the peak intensity is small. If it is true, the hybridization effect is quite strong even in the case of UGa$_2$ which has been regarded as a typical localized system. Anyhow, the results of the present experiments indicate that it may not be appropriate to apply the simple crystal field model to these systems.

For UGa$_2$, well defined spin wave excitations were observed below $T_C$. The observed dispersion relation reflects the magnetic anisotropy in this system. The excitations show the dispersion of about 4 meV along [0,0,1] direction, however, it is almost constant in the (0,0,1) plane. This indicates that the exchange interaction in the c-plane is quite small compared to that along c-axis.

The reason of the failure to detect the spin wave excitation in UGe$_2$ is not clear. However, it may be considered that the cross section for the spin wave scattering is small in the case of UGe$_2$ since its ordered magnetic moment is about half that of UGa$_2$. More detailed study using a large single crystalline sample of UGe$_2$ is in progress.
ACKNOWLEDGEMENTS

This work was partly supported by the Iketani Science and Technology Foundation.

REFERENCES

SAMPLE DEPENDENCE OF MAGNETIC ORDERING IN THE YTTERBIUM MONOPNICTIDES YbN AND YbP

A. DÖNNI1, L. KELLER2, P. FISCHER2, A. FURRER2, M. KOHGI1 and T. SUZUKI1

1 Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan
2 Laboratory of Neutron Scattering, ETH Zürich, CH-5232 Villigen PSI, Switzerland

With respect to the competition between Kondo hybridization and magnetic interactions the ytterbium monopnictides are of particular interest. Recently magnetic ordering of stoichiometric samples of YbX (X= N, As, Sb) and nonstoichiometric YbP0.84 prepared at ETH Zürich were investigated by neutron scattering techniques [1]. At TN = 0.79 K stoichiometric YbN showed an antiferromagnetic fcc type-III structure with a small ordered magnetic moment of μYb = 0.39(5) μB. In nonstoichiometric YbP0.84 fcc type-II antiferromagnetism with μYb = 1.03(7) μB was observed below TN = 0.64 K. According to Mössbauer experiments [2] both samples undergo first-order phase transitions with a small range of coexistence between paramagnetism and antiferromagnetism of less than 0.1 K in YbN and about 0.15 K in YbP0.84.

Now we used powder samples of YbN and YbP prepared at Tohoku University and performed new dilution powder neutron diffraction experiments on spectrometer DMC [3] at reactor Saphir in Würenlingen, Switzerland. By analyzing paramagnetic neutron diffraction patterns both samples Yb1-xN and Yb1-xP were found to be stoichiometric with x = z = 0.99(1). Both new samples exhibit the previously observed kind of antiferromagnetic structures. In YbN we find fcc type-III antiferromagnetism with an ordered saturation moment of μYb = 0.52(6) μB, and YbP shows fcc type-II antiferromagnetism with μYb = 0.89(6) μB. The temperature dependence of the magnetic neutron intensities shows a strong sample dependence. In the new stoichiometric YbN sample the first-order phase transition is smeared out in the sample between 0.35 K and 0.80 K and the sample quality is inferior to the previously investigated stoichiometric YbN sample. On the other hand compared to the nonstoichiometric YbP0.84 the new stoichiometric YbP sample has a much sharper first-order phase transition at a slightly higher Néel temperature of 0.66 K. We find that for YbN and YbP higher quality samples show sharper first-order phase transitions at higher Néel temperatures. However, the kind of the antiferromagnetic structure is not sensitive to the sample quality.

SOFT MODES AND PHASE TRANSITION AT 74K IN Rb$_2$ZnCl$_4$

$^1$Hiroyuki MASHIYAMA, $^1$Kousirou SUGIMOTO, $^2$Yasuaki OOHARA 
and $^2$Hideki YOSHIZAWA

$^1$Department of Physics, Faculty of Science, 
Yamaguchi University, Yoshida 1677-1, Yamaguchi, 753 Japan

$^2$Institute for Solid State Physics, 
University of Tokyo, Roppongi, Minato-ku, Tokyo, 106 Japan

ABSTRACT

The orthorhombic to monoclinic transition at $T_m=73.5$K in Rb$_2$ZnCl$_4$ is investigated by means of neutron scattering at JRR-3M. The superlattice reflections observed below $T_m$ increases as $(T_m-T)^{2.3}$ with $\beta=0.38$. The dispersion relations of low energy are determined both above and below $T_m$. The softening of phonon frequency is observed around the Brillouin zone-boundary. The square of the energy transfer of the soft phonon obeys a linear relation on temperature.

INTRODUCTION

Rubidium tetrachrolozincate, Rb$_2$ZnCl$_4$, is one of the A$_2$BX$_4$ type ferroelectrics$^1$ that performs the normal-incommensurate and incommensurate transitions. Phase 1 is the normal phase with the space group Pmcn (Z=4). With decreasing temperature, the crystal transforms to the incommensurate and the commensurate phases successively at 303K and 193K. The commensurate phase 3 is ferroelectric along the $\alpha$-axis. The space group is P2$_1$cn (Z=12). The cell dimension along the $c$-axis is three times the basic cell length of the normal phase 1.

The A$_2$BX$_4$-type crystals are known to make another phase transition at a lower temperature $T_m$, below which the cell size is doubled.$^{2,3}$ In Rb$_2$ZnCl$_4$, $T_m$ is reported as 74K.$^3$ In K$_2$CoCl$_4$ and K$_2$ZnCl$_4$, the space group of the monoclinic phase 4 is C1c1 (Z=48).$^4$ It is reported that an intermediate incommensurate phase exists in K$_2$ZnCl$_4$ between phases 3 and 4 by means of neutron scattering.$^5$

Since the orthorhombic to monoclinic transition is common in A$_2$BX$_4$-type crystals, the transition has been widely investigated.$^6$ Soft phonon mode with vanishing frequency at $T_m$ was first observed by Raman scattering.$^3,7$ Recently neutron inelastic scattering has been performed and the soft modes have been observed in the ferroelectric phase 3 above $T_m$.$^8$

In order to clarify the mechanism of the orthorhombic to monoclinic transition at $T_m$, we investigate Rb$_2$ZnCl$_4$ by neutron scattering experiments. The superlattice reflections appear at $(\xi \eta 0)$ where $\xi$ and $\eta$ are half integers in phase 4. The observed reflection condition within the 1=0 layer is consistent with the space group C1c1 as same as in K$_2$CoCl$_4$ and K$_2$ZnCl$_4$.$^6$ The critical index $\beta$ is estimated from the temperature dependence of the superlattice reflections. The dispersion relations of low energy phonon
have been determined along the \((\xi - \xi 0)\) direction both in phases 3 and 4. The frequency at \((1/2 1/2 0)\) softens towards \(T_m\). Our results are complementary to the report by Quillichini et al. Some results of our experiments have been reported elsewhere. The experimental details are described in the next section. The results and the discussions are presented in the final section.

**EXPERIMENTAL**

Single crystal of Rb$_2$ZnCl$_4$ was grown by the Bridgman method by Dr. Hashimoto, Kyoto Educational University. The obtained whole block was a colorless and transparent single crystal. Neutron scattering experiments were performed by the use of triple-axis spectrometers TAS(4G) and HER(C1-1), installed at the reactor hall and the guide hall at JRR-3M in JAERI. A crystal with a size of 2x1x1.4 cm$^3$ was mounted in an aluminum can and set in a cryostat which was cooled by cryogenics. The temperature was controlled within 0.1K by a personal computer. The measurement process was remote-controlled via a computer in the building next to the reactor hall.

The Bragg peak width (FWHM) was less than 0.5’ in 10’-40’-40’-open collimation. Normal energy scans were made with fixed incident neutron momentum \(k_i=2.87\)A$^{-1}$ in 40’-40’-40’-40’ collimation within the \((\xi \eta 0)\) scattering plane. Here the reciprocal lattice units refer to the unit cell of phase I with space group Pmnc; lattice parameters \(a=7.28\)A, \(b=12.72\)A & \(c=9.22\)A at room temperature. Higher resolution was achieved by HER with the use of cold neutron. The incident neutron momentum was \(k_f=1.55\)A$^{-1}$ in open-open-80’-80’ collimation.

**RESULTS AND DISCUSSIONS**

A general survey of quasi-elastic scattering along the \(x’\)-axis across a reciprocal point \((2.5 1.5 0)\) is shown in Fig. 1. Strong diffuse scattering is observable around the zone-boundary point. From the temperature dependence of the diffuse intensity, the transition temperature \(T_m\) is determined to be 73.5K.

![Fig. 1. Scattering intensity at \((\xi 1.5 0)\) scanned around \(\xi=2.5\). Counting time for 128K is twice the others.](image-url)
The peak intensity at (2.5 0.5 0) is shown in Fig. 2 as a function of temperature. The temperature dependence is fitted to a power law and the critical index for the order parameter is estimated as β=0.38. If the integrated intensity of the (3.5 4.5 0) reflection is fitted, β is estimated as 0.36.\(^9\)

Superlattice reflections are observed at the zone boundary where both ξ and η are half integers. If ξ+η is a half integer, then no Bragg reflection is observable. This reflection condition is consistent with the space group Ccl1. The strong superlattice reflections are (2.5 0.5 0), (2.5 1.5 0), (3.5 4.5 0) and (0.5 4.5 0). These are in agreement with the calculated structure factors based on the parameters of phase 4 (space group Ccl1) of K₂CoCl₆.

![Graph](image)

**Fig. 2.** The temperature dependence of a superlattice reflection. The solid curve shows the fitted relation to a power law.

The inelastic neutron scattering intensity was mainly investigated on the lines (4 4 0)-(3 5 0) and (1 4 0)-(0 5 0). On the former line, the reflection at (3 5 0) was strong and an acoustic branch was observed. On the latter line, an optical phonon was observable because (1 4 0) and (0 5 0) were forbidden in the orthorhombic phase 3. For both cases, phonon propagation vector q was nearly perpendicular to scattering vector Q. Therefore transverse modes were mainly detected. The typical resolution (HWHM) was 0.6meV for soft phonon or 0.4meV for incoherent scattering.

In order to get better resolution, cold neutron was also used. In this case, the wavelength is longer and the Q-vector is limited. Therefore the line (2 2 0)-(3 1 0) was investigated instead of the line (4 4 0)-(3 5 0).

In Fig. 3, an energy scan with constant Q at (2.5 1.5 0) is shown, where cold neutron is used. The HWHM of the incoherent scattering around zero energy transfer is 0.12meV. The phonon peak shifts to lower energy with decreasing phonon wave vector q. This mode is identified as the soft mode reported by Quilichini et al.\(^9\)
The dispersion relation of the low energy mode in the extended zone scheme is plotted in the $(\xi - \xi 0)$ direction in Fig. 4 for phase 3. At the zone boundary $(0.5 0.5 0)$, the acoustic mode $(\xi < 0.5)$ and the optical mode $(\xi > 0.5)$ are degenerated. The dispersion relation in phase 4, which was obtained by energy scan around $Q=(3.5 4.5 0)$, was shown in Ref. 9.

Fig. 3. Scattering intensity with constant $Q$ scans around $(2.5 1.5 0)$ as a function of energy transfer for 78K observed by the use of cold neutron.

Fig. 4. Dispersion curves in extended zone scheme for the soft phonon mode along the $(\xi \xi 0)$ line in phase 3 of Rb$_2$ZnCl$_4$. Solid lines are guides for the eye. The dispersion for 295K are from ref. 8.
The square of the energy transfer for \( q = 0.05 \) and 0.1 is plotted against temperature in Fig. 5, where \( q \) is the relative wave vector from the zone-boundary point of phase 3. The four data at \( q = 0 \) above the transition temperature are those obtained by Quilichini et al.\(^8\) The soft Raman frequency of the \( A_1 \) mode in ref. 7 is shown by open circles. The whole dispersion relation clearly indicates that the zone boundary mode \( (\xi = 1/2) \) softens as the temperature approaches \( T_s = 73.5K \).

It was found in this study that the transition from the commensurate phase 3 to the monoclinic phase 4 is of the second order with the critical index \( \beta = 0.38 \). The observed reflection condition within the \( \zeta = 0 \) layer is consistent with the space group \( \text{C}1\text{c}1 \) in the monoclinic phase 4.

On the other hand, the commensurate to monoclinic transition in \( \text{K}_2\text{ZnCl}_4 \) is a discontinuous one at 145K. In this crystal weak satellite reflections are observed at \( (1/2-\delta 1/2 0) \) in a few degrees of temperature just above 145K.\(^5\) It is also reported that the phonon dispersion relation of \( \text{K}_2\text{ZnCl}_4 \) has a minimum at \( (1/2-\delta 1/2 0) \),\(^6\) in contrast to the zone-boundary point for the case of \( \text{Rb}_2\text{ZnCl}_4 \). This is considered to be the reason why the transition is the second order one in the rubidium compound.

![Fig. 5. Temperature dependence of square of the energy transfer of soft phonons. Data points from inelastic neutron scattering (80 - 101K) in ref. 8 and Raman scattering (20, 40K) in ref. 7 are shown by open circles.](image)

We have determined the full dispersion relation of the soft phonon. The softening is observed around the zone-boundary \((0.5 0.5 0)\). The soft phonon frequency decreases towards \( T_s \) with the square root relation in a wide temperature range for both phases 3 and 4. The width of the phonon peak, which is related to the damping constant, increases a little for small \( q \). If the phonon energy becomes comparable with the width, then the phonon spectrum becomes an overdamped shape around \( T_s \). It should be noted that such a region is narrow, and that soft phonon picture is well defined for the structural transition at 74K in \( \text{Rb}_2\text{ZnCl}_4 \).

The authors are indebted to Dr. Hashimoto for growing the single crystal.
REFERENCES


P-123

STRUCTURAL STUDY IN METALLIC SODIUM

H. ABE, K. OHSHIMA, T. SUZUKI, S. HOSHINO and *K. KAKURAI

Institute of Applied Physics, University of Tsukuba, Tsukuba 305, Japan

*Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

Metallic sodium undergoes martensitic phase transformation from bcc to 9R structure at 37 K (M_s). Blaschko observed phonon dispersion curves between 230 and 40 K by neutron inelastic scattering technique and found that the frequency in lowest branch TA_1[110] decreased about 4% near the zone boundary at 40 K. We have performed neutron elastic and inelastic scattering experiments from metallic sodium to understand more detailed structural informations.

The single crystal was prepared in liquid paraffin above the melting point (97 °C) and gradually cooled down to room temperature. The size of the specimen was 18 mm in diameter and the mosaic spread was 20°. The data were collected with the use of a triple-axis spectrometer at the beam line 5G of JRR-3M, JAERI. It was done under a constant incident neutron wave length λ = 2.35 Å, whose energy resolution was 0.87 meV. The temperature was changed with the use of closed cycle refrigerator and controlled within 0.1 degrees.

Phonon dispersion curves from 200 K to M_s were measured along high symmetry directions. There were no peculiar temperature changes for TA_1 [110] branch. The temperature dependence of integrated intensity and full width at half maximum (FWHM) was also obtained from the (110) bcc Bragg reflection. They were increased drastically at M_s due to the structural change which took place after an incubation time of the order of few hours. We also observed peculiar Huang scattering around the Bragg reflection. Above A_s, both the integrated intensity and FWHM were decreased where Huang scattering disappeared. It is thought that these phenomena are very important to understand the phase transformation in metallic sodium.
MAGNETIC ORDERING IN DELAFOSSITE-TYPE RHOMBOHEDRAL ANTIFERROMAGNETS

Mamoru MEKATA, Yoshitami AJIRO, Nariyasu YAGUCHI, Hideaki KURIYAMA, Takayuki ASANO, *Hiroaki KADOWAKI, *Yasuaki OOHARA, **Setsuo MITSUDA and *Hideki YOSHIZAWA

Department of Applied Physics
Faculty of Engineering, Fukui University
3-9-1 Bunkyo, Fukui 910, Japan

*Institute for Solid State Physics
University of Tokyo
7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

*Department of Physics
Science University of Tokyo
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

ABSTRACT

Magnetic ordering processes in CuCrO$_2$, AgCrO$_2$, CuFeO$_2$ and CuNdO$_2$ with the delafossite-type structure were studied by powder neutron diffraction. Owing to the frustration among moments on the rhombohedral lattice, each compound exhibits a characteristic ordering. The magnetic structures of CuCrO$_2$ and AgCrO$_2$ below 25K and 24K are helical in the c-plane with $Q=0.333$ and $Q=0.327$, respectively. The observed $Q$ distribution is attributed to the almost degenerate excited states with $Q$ near 0.327. CuFeO$_2$ exhibits a successive transition at 16K and 11K. The moments on 1/5 sites remain disordered in the intermediate temperature phase. The determined magnetic structures are successfully interpreted in terms of a classical Ising spin model. No long range ordering was observed down to 2K in CuNdO$_2$. 
INTRODUCTION

It is well known that magnetic moments on the triangular lattice are highly frustrated when they interact antiferromagnetically. Ising spin system exhibits no long range ordering down to 0K, but an additional interaction gives rise to a variety of orderings. In some cases, partially disordered structure of Kosterlitz-Thouless type may occur in an intermediate temperature phase associated with a successive transition.\(^1\) In Heisenberg spin systems with only the nearest neighbor interaction, any magnetic transition into a long range order can not be expected at finite temperatures but additional interaction yields mostly 120° spin structure, the helix with Q=0.333.\(^2\)

Rhombohedral stacking of antiferromagnetic triangular lattices retains the spin frustration regardless of the sign of the exchange interaction between the adjacent triangular planes. In some cases, helical spin configurations on the triangular planes may be incoherent with each other resulting in degenerate helices along the axis of the stacking.\(^3\)

Most of ABO\(_2\) compounds crystallize in delafossite-type or αNaFeO\(_2\)-type structures both of which have the rhombohedral lattice of magnetic B ions. The A ions of the 1b group in the periodic table form the delafossite-type crystals, while those of the 1a group form the αNaFeO\(_2\)-type crystals. Generally, αNaFeO\(_2\)-type compounds have some deficiency in A ions, whereas we have less problem of stoichiometry in delafossite-type compounds. Here we summarize the recent results of the powder neutron diffraction experiments on CuCrO\(_2\), AgCrO\(_2\), CuFeO\(_2\) and CuNdO\(_2\).

EXPERIMENTALS

The neutron diffraction was measured in two axis mode with the ISSP ND-1 and the ISSP 4G spectrometers installed at JRR2 and JRR3, JAERI Tokai. Mostly, neutrons with wave length of 2.4436Å were utilized.

The samples except AgCrO\(_2\) were prepared from their constituent oxide powder by solid state reaction in an appropriate atmosphere. In the case of AgCrO\(_2\), the starting materials are Ag and Cr\(_2\)O\(_3\). The X-ray diffraction lines of the prepared samples are sharp enough without extra line. Lattice constants of the prepared samples are in good agreement with the reported values.
RESULTS

CuCrO₂

Figure 1 shows powder diffraction patterns of CuCrO₂ measured at 9K and 32K. The magnetic reflections can be indexed in terms of (1/3 1/3 n) but they are appreciably broadened as compared with the nuclear peak widths indicating finite correlation along the c-axis. The observed intensity of the reflection is consistent with the 120° structure in the ac-plane with moment 3.1μB. The relative orientation of the moments among the stacked layers was hardly determined from the present data. The temperature dependence of the peak intensity of (1/3 1/3 0) reflection shows an anomaly at Tₙ=25K as seen in Fig.2. It should be noted that the prominent diffuse scattering is due to the two-dimensional short range ordering.

Fig.1 Powder diffraction pattern of CuCrO₂.

Fig.2 Temperature dependence (1/3 1/3 0) peak intensity of CuCrO₂.
AgCrO$_2$

Magnetic peaks in the powder pattern of AgCrO$_2$ are not so distinct as those of CuCrO$_2$ and can not be indexed in terms of the commensurate 120° structure in the c-plane but an incommensurate $Q=0.327$ structure as shown in Fig.3. The deformation from the 120° structure with $Q=0.333$ implies that the third neighbor interaction and/or the inter-plane interaction are sizable. It can be easily shown that in this situation the magnetic energy varies little with the $Q$ values compared with thermal energy giving rise to a temperature dependent distribution over various $Q$ states. Actually, the widths of the magnetic peaks decrease as temperature is lowered resulting in dissimilar temperature dependences of the peak intensities as shown in Fig.4. The $T_N$ deduced from the figure is 24K although the anomaly is less clear than that of CuCrO$_2$.

Fig.3 Powder diffraction pattern of AgCrO$_2$.

Fig.4 Temperature dependences of peak intensities of AgCrO$_2$. 
CuFeO$_2$

The powder diffraction patterns taken at 4.6K, 13.5K and 50K shown in Fig.5 indicate that CuFeO$_2$ has two magnetic ordered phases with different magnetic unit cells from each other commensurate with chemical unit cell.$^6$ The temperature dependences of the peak intensities of (1/4 1/4 1/2) and (1/5 1/5 1/2) reflections are shown in Fig.6 together with that of the diffuse scattering intensity which gives the transition temperatures of $T_{N1}$=16K and $T_{N2}$=11K. The $T_{N2}$ is of first order. The magnetic structure deduced from the pattern is illustrated in Fig. 7. The magnetic structure of the

Fig.5 Powder diffraction patterns of CuFeO$_2$.

Fig.6 Temperature dependences of magnetic intensities of CuFeO$_2$. 

---

331
Intermediate temperature phase is characterized by disordering of 1/5 sites. The Mössbauer effect\(^7\) and \(\mu^+\)SR\(^9\) give experimental evidences for the partially disordering. An Ising spin model was successful to interpret the observed successive transition in terms of the competition among the exchange interactions extending up to the third neighbor.\(^7,\)\(^9\)

(a) Low temperature phase (b) Intermediate temperature phase

Fig. 7 Magnetic structures of CuFeO\(_2\).

CuNdO\(_2\)

Figure 8 shows the powder diffraction patterns of CuNdO\(_2\).

Fig. 8 Powder diffraction patterns of CuNdO\(_2\).
Neither coherent nor incoherent magnetic scattering was observed down to 2K as seen more clearly in Fig. 9 where nonmagnetic contribution was subtracted by the 50K pattern. Judging from the transition temperature 0.6K determined by heat capacity measurements\textsuperscript{9}, the exchange interaction in CuNdO\textsubscript{2} is expected to be very weak.

Fig.9  Magnetic diffraction patterns obtained by subtraction of 50K pattern.

DISCUSSIONS

As expectedly, the studied ABO\textsubscript{2} compounds exhibit characteristic magnetic ordering processes due to competition among the exchange interactions at least up to the third neighbor interaction in addition to the interplane interaction. The variety of the ordering processes may be attributed to the fact that the first neighbor interaction is not predominant over further interactions. Weak critical divergence is another feature; the sloppy ordering is a consequence of the frustrations in the systems.

ACKNOWLEDGEMENT

Authors would like to thank Mr. Y.Kawamura for his technical assistance throughout this work.
REFERENCES

5) Y.Oohara, S.Mitsuda, H.Yoshizawa, N.Yaguchi and M.Mekata: to be published.
UNIVERSALITY CLASSES OF MAGNETIC PHASE TRANSITIONS IN THE STACKED TRIANGULAR LATTICE ANTIFERROMAGNETS, CsMnBr₃ and CsMnI₃

Yoshitami AJIRO and *Hiroaki KADOWAKI

Department of Applied Physics, Fukui University
Bunkyo, Fukui 910, Japan

*Institute for Solid State Physics, The university of Tokyo
Minato-ku, Tokyo 106, Japan

ABSTRACT

Our recent results of the neutron scattering study on new universality classes of magnetic phase transitions in the stacked triangular lattice antiferromagnets, CsMnBr₃ and CsMnI₃ are summarized. For CsMnBr₃ with XY spin symmetry a new phase transition characterized by the novel critical exponents $\beta=0.25(1)$, $\gamma=1.10(5)$ and $\nu=0.57(3)$ was found in good agreement with the prediction for $Z_2 \times S_1$ or O(2) symmetry order parameter, giving an experimental evidence for the existence of a new universality class linked to chiral symmetry. A comparative study on an isomorphic compound CsMnI₃ with Ising spin symmetry has revealed that the exponents, $\beta_{//}=0.32(1)$ and $\beta_{\perp}=0.35(1)$ for the orderings of the parallel and perpendicular spin components to the c-axis definitely differ from that for CsMnBr₃ and much closer to theoretical $\beta=0.345$ for the XY symmetry of the order parameter despite the fact the spin has an Ising symmetry. However, the exponents, $\gamma_{//}=1.12(7)$, $\nu_{//}=0.59(3)$ and $\gamma_{\perp}=1.04(3)$, $\nu_{\perp}=0.56(2)$ do not show a meaningful difference from those of CsMnBr₃ within the experimental errors and are not consistent with the expected XY universality.
INTRODUCTION

Ordering phenomena are classified to universality classes by symmetry of order parameter and spatial dimensionality. As for the magnetic transition, the symmetry of order parameter is usually governed just by spin symmetry of a single spin on the lattice point. Here, we are interested in a new universality class in which the magnetic ordering is characterized by the whole symmetry of the order parameter instead of just spin symmetry. Kawamura [1] has predicted the existence of a new universality class linked to to chiral degeneracy inherent to the frustrated stacked triangular lattice antiferromagnet (TAL-AF). In three-dimensionally stacked TAL-AF with XY spin symmetry, the ground state has a continuous rotational degeneracy as well as a twofold discrete degeneracy specified by chirality, either right- or left-handed 120° structure. In terms of the topological description, the order parameter space has the $Z_2 \times S_1$ or $O(2)$ symmetry. For the stacked TAL-AF with Ising spin symmetry, a scaling theory [2] predicts that the phase transition belongs to the XY universality.

The purpose of the present paper is to elucidate the universality classes of magnetic phase transitions in the stacked TAL-AF's, CsMnBr$_3$ and CsMnI$_3$ from a comparative study of neutron scattering. Two compounds have the same hexagonal structure and almost the same magnetic parameters except the anisotropy which produces an essential difference in ordering phenomena. A weak XY anisotropy of CsMnBr$_3$ stabilizes the triangular structure with sublattice moments restricted in the basal c-plane below $T_N=8.42$ K while a weak Ising anisotropy of CsMnI$_3$ stabilizes the triangular structure in a plane perpendicular to the c-plane and splits the Néel temperature into two successive transitions, at $T_{N1}=11.2$ K and $T_{N2}=8.2$ K which correspond to ordering of magnetic moments parallel and perpendicular to the Ising c-axis, respectively.

EXPERIMENTALS

Neutron scattering experiments were performed in double-axis mode using the triple-axis spectrometers installed at JAERI (Tokai) and Brookhaven. A different run of measurements was also carried out at KUR (Kumatori). The neutron energy and the collimation were selected appropriately in case by case and the quasi-elastic approximation was confirmed. Single crystals were grown by Bridgeman method. Each sample with a very small mosaic spread less than 10' was mounted in a cryostat with the [110] axis vertical so as to measure the scattering in the (h,h,l) zone of the reciprocal lattice. The temperature of the specimen was measured with a Si diode or a Ge resistance thermometer and controlled within 0.001 K.
RESULTS

CsMnBr$_3$

In order to determine the critical exponent $\beta$, intensities of several magnetic reflections were measured as a function of temperature. No appreciable secondary extinction effect was observed in the magnetic Bragg reflections judging from the temperature independence of the ratios among (1/3,1/3,1), (2/3,2/3,1) and (4/3,4/3,1) peak intensities. The Bragg intensity of (1/3,1/3,1) reflection was carefully measured using scans along (h,h,1) to subtract the critical scattering. The obtained results were plotted as a function of the reduced temperature, $\varepsilon=(T_N-T)/T_N$, in a log-log plot as shown in Fig.1. The data was best fitted to the relation,

$$I_{\text{Bragg}} \propto (T_N-T)^{2\beta}$$

with $T_N=8.42(5)$ K and $\beta=0.25(1)$. Thus, we obtained [3] the critical exponent, $\beta=0.25(1)$ in the rather wide temperature range $0.003 < \varepsilon < 0.1$.

![Log-log plot of the magnetic Bragg intensity of the (1/3,1/3,1) reflection as a function of reduced temperature.](image_url)

In Fig. 2 the staggered susceptibility $\chi_s$ and the inverse correlation length $\kappa$ are shown as a function of reduced temperature. As seen from this figure, a rounding of the critical divergence occurs in the
temperature range $\epsilon'=(T-T_N)/T_N < 0.01$. The maximum correlation lengths in this sample are 9.5a and 130c in the c-plane and along the c axis, respectively. Because of the long correlation lengths parallel to the c-axis, some defects may give rise to the rounding for relatively large $\epsilon'$. We obtained [4] the exponents, $\gamma=1.10(5)$ and $\nu=0.57(3)$ from the data in the temperature range $0.015 < \epsilon' < 0.1$ by fitting to power law with fixed $T_N$.

![Graphs showing susceptibility and inverse correlation length](image)

Fig. 2. Log-log plot of staggered susceptibility $\chi_s$ (a) and inverse correlation length $\kappa$ (b) as a function of reduced temperature.

CsMnI$_3$

The temperature dependence of the peak intensity of (1/3,1/3,1) magnetic reflection is shown in Fig. 3. Two phase transitions are clearly seen at $T_{N1}=11.20\text{K}$ and $T_{N2}=8.17\text{K}$ as indicated by arrows. These successive transitions correspond to magnetic ordering of parallel and perpendicular spin components to the Ising c-axis, $S_\|$ and $S_\perp$, respectively. Using the observed intensities of two Bragg reflections, (1/3,1/3,1) and (2/3,2/3,1), we properly separated the contributions of $S_\|$ and $S_\perp$ from each other and confirmed that the perpendicular component $S_\|$ vanishes at $T_{N2}$. In the intermediate phase ($T_{N1}>T>T_{N2}$) only the c-axis spin component orders while the perpendicular c-plane component orders below $T_{N1}$. The critical
exponents for the parallel and perpendicular components were determined [5] to be $\beta_{\parallel}=0.32(1)$ and $\beta_{\perp}=0.35(1)$, respectively, as shown in Fig. 4.

![Graph showing temperature dependence of Bragg peak intensity](image1)

**Fig. 3.** (left) Temperature dependence of the peak intensity of the (1/3,1/3,1) magnetic Bragg reflection. Two phase transitions are clearly seen at $T_{\text{N1}}=11.2$ K and $T_{\text{N2}}=8.17$ K as indicated by arrows.

![Graph showing log-log plot of c-axis and c-plane components](image2)

**Fig. 4.** (right) Log-log plot of the c-axis (parallel) and c-plane (perpendicular) component of square of sublattice moment as a function of reduced temperature.

In order to determine the temperature dependence of wave-vector dependent susceptibility, we carefully measured the intensities of diffuse scattering around (1/3,1/3,3) and (2/3,2/3,1) reflections by scanning along (h,h,3) and (h,h,1) lines. After a proper substraction of the Bragg contribution we decomposed $X_{\parallel}(Q)$ and $X_{\perp}(Q)$, using the procedure mentioned in ref.[6]. Four critical exponents, $\nu_{\parallel}=1.12(7)$, $\nu_{\perp}=1.04(3)$, $\gamma_{\parallel}=0.59(3)$ and $\gamma_{\perp}=0.56(2)$ were [6] obtained by fitting the staggered susceptibilities, $X_{s\parallel}$ and $X_{s\perp}$, and inverse correlation lengths, $\kappa_{\parallel}$ and $\kappa_{\perp}$, to power law in the temperature range $0.007 < \varepsilon'(T_{\text{N1}}) < 0.2$, as shown in Figs. 5 and 6.
Fig. 5. Log-log plot of staggered susceptibility $\chi_{s//}$ (a) and inverse correlation length $\kappa_{s//}$ (b) as a function of reduced temperature.

Fig. 6. Log-log plot of staggered susceptibility $\chi_{s\perp}$ (a) and inverse correlation length $\kappa_{s\perp}$ (b) as a function of reduced temperature.

DISCUSSION AND CONCLUSIONS

We have determined the critical exponents, $\beta$, $\gamma$ and $\nu$ of the magnetic phase transitions in CsMnBr$_3$ and CsMnI$_3$ which are isomorphic compounds with almost the same magnetic parameters except the anisotropy producing an essential difference in ordering phenomena. These critical exponents are now compared with the
Theoretical prediction. Theoretical critical exponents of the various three-dimensional models are listed in Table I together with the available experimental data [5-7].

Table I. Theoretical and experimental critical exponents for three-dimensional models

<table>
<thead>
<tr>
<th>order parameter</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ising</td>
<td>0.106</td>
<td>0.3260</td>
<td>1.2378</td>
<td>0.6312</td>
</tr>
<tr>
<td>XY</td>
<td>-0.01</td>
<td>0.345</td>
<td>1.316</td>
<td>0.669</td>
</tr>
<tr>
<td>Heisenberg</td>
<td>-0.121</td>
<td>0.367</td>
<td>1.388</td>
<td>0.707</td>
</tr>
<tr>
<td>SO(3)</td>
<td>0.34</td>
<td>0.28</td>
<td>1.10</td>
<td>0.55</td>
</tr>
<tr>
<td>$Z_2 \times S_1$</td>
<td>0.40</td>
<td>0.25</td>
<td>1.10</td>
<td>0.53</td>
</tr>
<tr>
<td>CsMnBr$_3$</td>
<td>$0.39(9)^{[8]}$</td>
<td>$0.25(1)^{[3]}$</td>
<td>$1.10(5)^{[4]}$</td>
<td>$0.57(3)^{[4]}$</td>
</tr>
<tr>
<td></td>
<td>$0.40(5)^{[9]}$</td>
<td>$0.22(2)^{[7]}$</td>
<td>$1.01(8)^{[7]}$</td>
<td>$0.54(3)^{[7]}$</td>
</tr>
<tr>
<td>CsMnI$_3$</td>
<td>$(T_{N1})$</td>
<td>no data</td>
<td>$0.32(1)^{[5]}$</td>
<td>$1.12(7)^{[6]}$</td>
</tr>
<tr>
<td></td>
<td>$(T_{N2})$</td>
<td>no data</td>
<td>$0.35(1)^{[5]}$</td>
<td>$1.04(3)^{[6]}$</td>
</tr>
</tbody>
</table>

As discussed in the introduction, it is predicted that the phase transition in CsMnBr$_3$ belongs to the novel $Z_2 \times S_1$ class while both the phase transitions in CsMnI$_3$ belongs to the conventional XY class. One can see from Table I that the experimental data for CsMnBr$_3$ are in excellent agreement with the theory. Recent measurements [8,9] of the specific heat exponent, $\alpha$ give a strong confidence for this argument, as also listed in Table I. Using these experimental exponents we can confirm the scaling relations, $\alpha+2\beta+\gamma=2$ and $\alpha=2-d\nu$ with $d=3$. We further note the fact that the phase boundaries in the temperature-field phase diagram of CsMnBr$_3$ can be well described [10] by the crossover exponents which agree with the theoretical prediction.

On the other hand, the results of CsMnI$_3$ are not consistent with the predicted XY universality. Although the $\beta$ exponents of CsMnI$_3$ definitely differ from that for CsMnBr$_3$ reflecting the different anisotropy between them and are closer to the XY value, the $\gamma$ and $\nu$ exponents for two substances do not show a meaningful difference within the experimental errors and much smaller than the XY values. In view of that the determined $\gamma$ and $\nu$ exponents nearly correspond to the SO(3) class, a possible origin is due to the rounding effect which prevents us from measurements sufficiently close to the XY transitions where the Ising spin symmetry dominates.
In conclusion, we have investigated the universality classes of the magnetic phase transitions in CsMnBr$_3$ and CsMnI$_3$ by measuring the critical exponents $\beta$, $\gamma$ and $\nu$ through neutron scattering experiments. For CsMnBr$_3$ with XY spin symmetry a new phase transition characterized by the novel critical exponents $\beta=0.25(1)$, $\gamma=1.10(5)$ and $\nu=0.57(3)$ was found in good agreement with the prediction for $Z_2\times S_1$ or $O(2)$ symmetry order parameter, giving an experimental evidence for the existence of a new universality class linked to $n=2$ chiral degeneracy. A comparative study on an isomorphic compound CsMnI$_3$ with Ising spin symmetry has revealed that the exponents, $\beta_f=0.32(1)$ and $\beta_0=0.35(1)$ for the orderings of the parallel and perpendicular spin components to the $c$-axis definitely differ from that for CsMnBr$_3$ and much closer to theoretical $\beta=0.345$ for the XY symmetry of the order parameter despite the fact the spin has an Ising symmetry. However, the exponents, $\gamma_f=1.12(7)$, $\gamma_0=0.59(3)$ and $\nu_f=1.04(3)$, $\nu_0=0.56(2)$ do not show a meaningful difference from those of CsMnBr$_3$ within the experimental errors and are not consistent with the expected XY universality. The origin of this discrepancy is not clear at present. Further investigations certainly are necessary.

ACKNOWLEDGEMENTS

We would like to thank the collaborators in references [3-6, 10] and the members of neutron facilities at Tokai, Brookhaven and Kumatori whose help was indispensable to this work. We also thank Professor H. Kawamura for valuable discussions. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

REFERENCES

MAGNETIC STRUCTURE OF Fe$_{1/3}$NbS$_2$

*T. SUZUKI, **S. IKEDA, ***J. W. RICHARDSON
and ****Y. YAMAGUCHI

*Institute of Physics
University of Tsukuba, Tsukuba-shi, Ibaraki 305, Japan

** Booster Synchrotron Utilization Facility
National laboratory for High Energy Physics
Tsukuba-shi, Ibaraki 305, Japan

***Intence Pulse Neutron Source
Argonne National Laboratory, Argonne, IL 60439-4814, USA

****Institute for Materials Research
Tohoku University, Sendai 980, Japan

ABSTRACT

Intercalated compound of Fe$_{1/3}$NbS$_2$ is known as an antiferromagnet with $T_N$ around 50K. In the present study the crystal and magnetic structure of re-examined using neutron diffraction. Though crystal structure is almost the same as the previous report, the magnetic is found to take another type of ordering compared with that of the previous report. Temperature dependence of the magnetization of Fe atom reveals the Ising character of this spin system.

INTRODUCTION

Layered transition-metal dichalcogenides MX$_2$ are interesting as it makes many materials by intercalating metal ions or small ion clusters. We are interested in the magnetic properties of transition metal ions intercalated in MX$_2$. In the case of Fe$^{2+}$ ions in MX$_2$ large magnetic anisotropy of Fe$^{2+}$ fixes the magnetic moment in the c-direction). We expected Ising spin behavior of this system, therefore we have measured the temperature dependence of the magnetic scattering, and
found a new set of the magnetic Bragg peaks contrary to the previous report 1).

EXPERIMENTAL

The compounds were synthesized from pure elements Fe, Nb and S. by solid state reaction. The mixed elements were sealed in a quartz tube in vacuum and heated at 850°C for two days. Temperature dependence of the magnetic susceptibility of the sample shows the Néel temperature being 47K, which is almost same to the previous value of 50K. Crystal structure data was obtained using GPPD neutron diffraction spectrometer by the TOF method at IPNS. The spectrum obtained at 293K shown in Fig. 1. Magnetic scattering was measured mainly using KSD neutron diffractometer at JRR-3. Diffraction pattern at 10K is shown in Fig. 2, and the magnetic Bragg peaks are indexed on the bases of the orthohexagonal unit cell with the dimnsion a*\sqrt{3}a*c.

![Diffraction spectrum by TOF method and Rietveld fitting at 293K.](image)

<table>
<thead>
<tr>
<th></th>
<th>B. Van Laar et al.</th>
<th>present experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.7685 (3)</td>
<td>5.7674 (3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>12.2056 (8)</td>
<td>12.1739 (1)</td>
</tr>
<tr>
<td>N(2c)</td>
<td>0.922 (6)</td>
<td>0.828 (5)</td>
</tr>
<tr>
<td>N(2d)</td>
<td>0.026 (5)</td>
<td>0.00</td>
</tr>
<tr>
<td>N(2b)</td>
<td>0.019 (5)</td>
<td>0.064 (5)</td>
</tr>
<tr>
<td>x</td>
<td>0.323</td>
<td>0.297</td>
</tr>
<tr>
<td>Z(4f)</td>
<td>0.9987 (2)</td>
<td>0.998 (1)</td>
</tr>
<tr>
<td>x(12i)</td>
<td>0.6717 (17)</td>
<td>0.6707 (9)</td>
</tr>
<tr>
<td>y(12i)</td>
<td>0.0014 (11)</td>
<td>0.0094 (45)</td>
</tr>
<tr>
<td>z(12i)</td>
<td>0.1292 (3)</td>
<td>0.1291 (14)</td>
</tr>
</tbody>
</table>

Table 1 The comparison between structural parameters obtained by the experiments by B. Van Laar et al. and present authors.
Fig. 2 Diffraction spectrum by a constant wave length type spectrometer.

RESULTS and DISCUSSION

On the crystal structure the results of the Rietvelt fitting to the spectrum shown in Fig. 1 are listed in Table 1. All parameters are almost the same as those in the previous report\(^1\)). On the other hand the magnetic scattering is different from the previous report, and it is explained with the magnetic structure shown in Fig. 3 which is so called "1st kind" ordering of orthorhombic lattice.\(^3\)) About the magnetic coupling of this structure, 2/3 of
6 nearest neighbors in c-plane are antiparallel, and 2/3 of 6 next nearest neighbors out of c-plane are also antiparallel to the central spin. These situations are the same as the magnetic structure proposed in the previous report. Interactions with the third and more distinct neighbors are different between two structure. The main source of the difference is thought to be different concentration of intercalated Fe ions as shown in Table I. The temperature dependence of magnetic peak intensity is characteristic as shown in Fig. 4. From the Mössbauer effect experiment, the valence of Fe atom is considered to be 2+. Therefore the magnetic moment contributed by spin is 4 μB. Then the temperature dependence of the magnetic peak intensity is expected to be consistent with the calculation S=2. But in this compound the dependence is consistent with the calculation S=1/2. This result shows the Ising character of Fe spin because of the large magnetic anisotropy.

![Graph](image)

Fig. 4 The temperature dependence of (0,1,1) magnetic peak intensity. Dotted and solid line denote calculation for S=2 and 1/2, respectively.

References
SYNTHESIS, STRUCTURE AND ELECTRICAL PROPERTIES OF THE THALLIUM RUTENATE PYROCHLORES

Ryoji KANNO, Jinfan HUANG* and Auther W. SLEIGHT*

Department of Chemistry
Faculty of Science, Kobe University
Kobe, Hyogo–ken, 657 Japan

*Department of Chemistry,
Oregon State University
Corvallis, OR, 97330 USA

ABSTRACT

The thallium ruthenate pyrochlores, $\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$, were synthesized and their structures were determined by neutron diffraction measurements. The low-temperature (LT) and high-temperature (HT) phases were obtained at reaction temperatures of 500 and 900°C, respectively. Neutron diffraction measurements indicated the compositions of $\text{Tl}_2\text{Ru}_2\text{O}_7$ and $\text{Tl}_2\text{Ru}_2\text{O}_{7.71}$ for the HT phase and the LT phase, respectively. Electrical resistivity measurements showed metallic property for the HT phase and semiconducting property for the LT phase. The relationship between the electrical properties and the structural changes is discussed.

INTRODUCTION

The pyrochlore ruthenates are technologically important materials as catalyst, electrocatalyst, and conducting component in thick-film resistors. Their electronic properties are of intrinsic interest, since the Ru 4d electrons are on the borderline between localized and itinerant behavior. For example, the bismuth ruthenate $\text{Bi}_2\text{Ru}_2\text{O}_7$ and the lead ruthenate $\text{Pb}_2\text{Ru}_2\text{O}_{7.5}$ are metallic Pauli paramagnets with a nearly temperature-independent resistivity, whereas the rare-earth ruthenates $\text{Ln}_2\text{Ru}_2\text{O}_7$ ($\text{Ln} = \text{Pr} - \text{Lu}$) and $\text{Y}_2\text{Ru}_2\text{O}_7$ are all semiconductors with a spontaneous ruthenium atomic moment$^{1,2,3}$. The thallium pyrochlore was first synthesized by Sleight et al. under 3 kbar of supporting pressure$^7$. $\text{Tl}_2\text{Ru}_2\text{O}_7$ showed metallic property with nearly temperature independent resistivity. Later, Jarrett et al. have reported that $\text{Tl}_2\text{Ru}_2\text{O}_{7.4}$ synthesized under high pressure showed a metallic-semiconducting transition around 120 K, and that the transition temperature varied with the amount of oxygen vacancy$^9$. However, no information about the structure has been reported. In the present study, we synthesized the thallium pyrochlores under atmospheric pressure and determined their structures using neutron diffraction measurements.

EXPERIMENTAL

The ternary oxide $\text{Tl}_2\text{Ru}_2\text{O}_{7.4}$ was prepared by heating an appropriate molar ratios of $\text{RuO}_3$, $\text{Ru}$, and $\text{Tl}_2\text{O}_3$ ($\text{RuO}_3$: Furüüchi Chemicals. Ltd., >99.99% purity; $\text{Tl}_2\text{O}_3$: Johnson Matthey, >99.999% purity; $\text{Ru}$: Johnson Matthey, >99.95% purity). They were mixed,
pelletized, sealed in an Ag tube, and then heated in the range of 500 – 900 °C. Oxidizing agents were used for increasing oxygen pressure in the tube (KO.: Johnson Matthey, >96.5% purity; KClO₃, Spectrum Chemical MFG. CORP.). Evacuated SiO₂ and Pyrex tubes were also used for reactions below 600°C. No reaction between the samples and the containers was observed at a reaction temperature of 500°C. Reactions were also carried out under oxygen gas flow, under nitrogen gas flow, or in air.

X–Ray diffraction (XRD) patterns of the powdered samples were obtained using a XR diffractometer (Simens D–5000) with CuKα radiation and a scintillation detector. The lattice parameters were measured using Si as an internal standard.

Neutron powder diffraction data were collected on the diffractometer on the beam line H4S of HFBR at Brookhaven National Laboratory. Data were collected in the angular range of 5° ≤ 2θ ≤ 120° using a wavelength of 1.358 Å and a 2θ step size of 0.1° at room temperature. About 10g of the sample was pressed into a pellet with 3/4" diameter and exposed to the neutron beam without using any containers. The data collection lasted for 24 h for each data set. The data were analyzed with the Rietveld method using the GSAS program. No collections for extinction or absorption were applied.

The electrical resistivity was measured for the sintered materials with dimensions of approximately 2 x 2 x 5 mm. The data were obtained by the a.c. four–probe method in the temperature range 77 ≤ T ≤ 300 K using a Lake Shore susceptometer MODEL 7000 with electrical conductivity measurement unit. The reaction and weight loss of the pyrochlores on heating up to 700°C were measured by an automatic differential thermal analysis–thermogravimetry (DTA–TG) apparatus of NETZSCH STA 409.

RESULTS AND DISCUSSION

Synthesis

The lattice parameters of the samples synthesized in this study varied from 10.1909 to 10.225 Å depending on their starting compositions and synthesizing conditions. Figure 1 shows the lattice parameters as a function of reaction temperature. This indicates that higher the reaction temperature, lower the lattice parameter. Figure 2 shows X-ray diffraction patterns for the samples synthesized in a sealed Ag-tube at 500 – 900 °C with a starting composition of Tl₂Ru₂O₇. The broad peaks were observed for the samples synthesized below 700 °C. The diffraction peaks at higher angles for the samples synthesized at 600 and 700 °C showed peak splitting which might be due to a low angle broad reflection and a high angle sharp reflection. The samples synthesized at 600 and 700 °C were mixtures of the low–temperature phase(LT) and the high–temperature phase(HT).

![Fig. 1. Reaction temperature dependence of lattice parameters for Tl₂Ru₂O₇-δ.](image1)

![Fig. 2. X-ray diffraction patterns for Tl₁Ru₂O₇-δ synthesized at 500, 600, 700, and 900°C.](image2)
Structure

$\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$ (LT)

Monophasic property of $\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$ (LT) was obtained by the reaction at 500°C either in a sealed Ag–tube or in an evacuated Pyrex–tube. The lattice parameter obtained in a sealed Ag–tube (10.2219(6) Å) is slightly larger than that obtained in a Pyrex–tube (10.2150(6) Å), indicating a certain range of solid solution in the system. The thallium pyrochlores have been reported to have lattice parameters in the range of 10.174 – 10.202 Å, when synthesized at 700 – 900°C and 3 – 30 kbar in a sealed gold ampule$^{5,6}$. Lower reaction temperatures examined in the present study lead to larger lattice parameters for the Ti pyrochlores.

The powdered sample for the structure determination was synthesized in an evacuated Pyrex–tube at 500°C for 1 week. Neutron diffraction intensity data between 10.00 and 120.00° were used for Rietveld analysis, but those in regions, 24.00–25.20, 35.00–36.50 and 60.00–60.90° were excluded in the refinement owing to the appearance of very weak peaks due to RuO$_2$. No (420) reflection was observed both in the neutron and X–ray diffraction data, indicating no vacancy ordering on the O' site$^7$. Refinement of the structure therefore proceeded with space group Fd3m with the structural model as follows: Ti, 16d (1/2, 1/2, 1/2); Ru, 16c (0, 0, 0); O(1), 48f (x, 1/8, 1/8), x = 0.327; O(2), 8b (3/8, 3/8, 3/8). When the occupation parameters, g, were allowed to vary for the Ti, O(1), and O(2) sites, these parameters tended to increase to values greater than 1.0. The occupation factors were therefore fixed at 1.0 for these sites. No correction for preferred orientation was made. The refinement using isotropic thermal parameters gave a Rwp value of 15.15%. Then, anisotropic thermal parameters were used for the final refinement. The refinement results are summarized in Table I(a). Figure 3(a) shows observed, calculated and difference plots for $\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$ (LT). Table II lists the interatomic distances and bond angles.

$\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$ (HT)

The powdered sample for the structure determination was synthesized in a sealed Ag–tube at 900°C for 2 h. The Ag–tube was then quenched into water. Neutron diffraction intensity data between 10.00 and 120.00° were used for Rietveld analysis. No impurity peaks were observed in the diffraction pattern. No (420) reflection in the neutron diffraction data indicates no vacancy ordering on the O' site. Refinement of the structure proceeded with space group Fd3m with the same model as that of the LT phase. When the occupation parameters, g, were fixed at 1.0 for each site, the B–value on the O(2) site tended to increase, which suggests the existence of oxygen vacancy in this site. The occupation factors, g, were therefore varied for the Ti and O(2) sites. The occupancy of the Ti site tended to increase to a value greater than 1.0; the g value for this site was fixed at 1.0. No correction for preferred orientation was made. The refinement using a constraint that the O(2) vacancy was related to the Ti vacancy was unstable. The refinement using isotropic thermal parameters gave a Rwp value of 20.31%. Then, anisotropic thermal parameters were used for the final refinement. The refinement results are summarized in Table I(b). Figure 3(b) shows observed, calculated and difference plots for $\text{Tl}_2\text{Ru}_2\text{O}_{7.5}$ (HT). Table II lists the interatomic distances and bond angles.

The neutron diffraction measurements revealed that the compositions of the thallium pyrochlores were $\text{Tl}_2\text{Ru}_2\text{O}_7$ and $\text{Tl}_2\text{Ru}_2\text{O}_{6.71}$ for the LT phase and the HT phase, respectively. In the HT phase, the oxygen vacancy of the amount of 0.29 might lead to a partial reduction of thallium from Ti$^{4+}$ to Ti$^+$. The average Ti–O distance of 2.4633 Å in the HT phase is larger than that of 2.4476 Å in the LT phase, consistent with the existence of larger Ti$^+$ ions (ionic radii; Ti$^{4+}$: 0.98 Å, Ti$^+$: 1.59 Å$^8$). On the other hand, the Ti–O(2) distance of 2.2109 Å in the LT phase is larger than 2.2085 Å in the HT phase. Smaller Ti–O(2) distance in the HT phase is explained by the existence of oxygen vacancy in the O(2) site. Smaller A–oxygen vacancy distance than the A–O distance has been previously reported for the lead pyrochlore Pb$_2$Ru$_2$O$_{6.5}$, where the oxygen vacancy ordered in the O' sites$^3$. Pb has been displaced significantly farther from the Fd3m symmetry position and each Pb atom is displaced by 0.040(4) Å toward its associated vacancy so that, along the <111> direction, the Pb–vacancy

— 349 —
Table I(a) Structural Parameters for Tl₂Ru₂O₇ (LT) in Fm̅3m

(a=10.2116(10) Å, R_p=13.92%, R_p=9.25%, R_e=11.29%, R_I=4.46%, R_F=3.85%)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>g</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B/A²(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>4a(1/2,1/2,1/2)</td>
<td>1.0</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.89</td>
</tr>
<tr>
<td>Ru</td>
<td>16c(0,0,0)</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.37</td>
</tr>
<tr>
<td>O(1)</td>
<td>48f(x,1/8,1/8)</td>
<td>1.0</td>
<td>0.3273(2)</td>
<td>1/8</td>
<td>1/8</td>
<td>1.58</td>
</tr>
<tr>
<td>O(2)</td>
<td>8b(3/8,3/8,3/8)</td>
<td>1.0</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.95</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁/Å²</th>
<th>U₂₂/Å²</th>
<th>U₃₃/Å²</th>
<th>U₁₂/Å²</th>
<th>U₁₃/Å²</th>
<th>U₂₃/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>0.0113(9)</td>
<td>0.0113</td>
<td>0.0113</td>
<td>-0.0033(7)</td>
<td>-0.0033</td>
<td>-0.0033</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0049(8)</td>
<td>0.0049</td>
<td>0.0049</td>
<td>-0.0018(8)</td>
<td>-0.0018</td>
<td>-0.0018</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0199(12)</td>
<td>0.0092</td>
<td>0.0092</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0072(13)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0139(19)</td>
<td>0.0139</td>
<td>0.0139</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table I(b) Structural Parameters for Tl₂Ru₂O₇-δ (HT) in Fm̅3m

(a=10.2089(8) Å, R_p=17.86%, R_p=10.37%, R_e=15.3%, R_I=4.55%, R_F=3.42%)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>g</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B/A²(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>4a(1/2,1/2,1/2)</td>
<td>1.0</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>0.75</td>
</tr>
<tr>
<td>Ru</td>
<td>16c(0,0,0)</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.39</td>
</tr>
<tr>
<td>O(1)</td>
<td>48f(x,1/8,1/8)</td>
<td>1.0</td>
<td>0.3235(3)</td>
<td>1/8</td>
<td>1/8</td>
<td>0.95</td>
</tr>
<tr>
<td>O(2)</td>
<td>8b(3/8,3/8,3/8)</td>
<td>0.71(2)</td>
<td>3/8</td>
<td>3/8</td>
<td>3/8</td>
<td>0.39</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>U₁₁/Å²</th>
<th>U₂₂/Å²</th>
<th>U₃₃/Å²</th>
<th>U₁₂/Å²</th>
<th>U₁₃/Å²</th>
<th>U₂₃/Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl</td>
<td>0.0095(9)</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0005(8)</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>Ru</td>
<td>0.0049(8)</td>
<td>0.0049</td>
<td>0.0049</td>
<td>-0.0013(9)</td>
<td>-0.0013</td>
<td>-0.0013</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.0120(11)</td>
<td>0.0086</td>
<td>0.0086</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0028(15)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.005(3)</td>
<td>0.005</td>
<td>0.005</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note. Numbers in parentheses are estimated standard deviations of the last significant digit, and those without deviations were fixed by the constraint.

The above refinement in Fm̅3m employed 22 variable parameters and 1150 degrees of freedom.
(a) Equivalent thermal parameters, B_eq.

Table II Interatomic distances and angles for Tl₂Ru₂O₇-δ.

coordinate triplets: i)x,y+1/2,z+1/2; ii)x=-1/4,y+1/4,-z; iii)x+1/4,-y+1/4,z; iv)x+1/4,y,-z+1/4; v)x,y+3/4,-z+3/4; vi)x+3/4,y, z+3/4; vii)x,y-1/2,z-1/2; viii)x+3/4,y,-z+3/4; viii)-x-1/4,y,-1/4.

<table>
<thead>
<tr>
<th>Phase</th>
<th>LT</th>
<th>HT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances</td>
<td>d / Å</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>-O(1)</td>
<td>2.5233(17)</td>
</tr>
<tr>
<td>Tl</td>
<td>-O(2)</td>
<td>2.21088(16)</td>
</tr>
<tr>
<td>Ru</td>
<td>-O(1ii)</td>
<td>1.9704(10)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th>θ / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ruiii</td>
<td>O(1)-Ruiv</td>
</tr>
<tr>
<td>Tlvi</td>
<td>-O(1)-Tlvii</td>
</tr>
<tr>
<td>Tlvi</td>
<td>-O(2)-Tlvii</td>
</tr>
<tr>
<td>O(1ii)-Ru</td>
<td>-O(1viii)</td>
</tr>
</tbody>
</table>
Fig. 3. Observed, calculated, and difference plots for the Rietveld refinement results. (a) LT phase; (b) HT phase.
distance is 2.180 Å while the Pb–O' distance is 2.260(2) Å.

Neutron diffraction measurements confirmed the oxygen vacancy in the Tl pyrochlore synthesized at higher temperatures, while no significant oxygen vacancy was observed in the pyrochlore synthesized at 500°C. The reaction in the sealed tubes is probably controlled by the gaseous species of thallium oxide, Tl₂O. Above 600°C, the following redox–vaporization process is well under way:\(^{9}\):  
\[ \text{Tl}_2\text{O}_3(s) \rightarrow \text{Tl}_2\text{O}(g) + \text{O}_2. \]

Tl₂O₃ melts at 717°C and its conversion to Tl₂O is complete at 875°C in air\(^{10}\). The stoichiometric Tl pyrochlore was obtained below a synthesis temperature where the redox–vaporization process is not significant. The DTA measurement for the sample synthesized at 500°C showed a small endothermic peak around 580°C accompanying a slight weight loss. This corresponds to a decomposition of the stoichiometric pyrochlore according to the following equation:  
\[ \text{Tl}_2\text{Ru}_2\text{O}_8 \rightarrow \text{Tl}_2\text{Ru}_2\text{O}_{8-d} + (d/2) \text{O}_2. \]

Further, heating at 900°C in open air has led to a complete decomposition from Tl₂Ru₂O₈ to RuO₂ and Tl₂O(g). High pressure technique is necessary to control the reaction at high temperatures.

Electrical properties

Figure 4 shows temperature dependence of the resistivity for Tl₂Ru₂O₈ synthesized in Ag–tube condition. Semiconducting property for the LT phase and metallic property for the HT phase were observed. No metallic–semiconducting transition was observed around 120K.

High pressure synthesis using reaction conditions of 3–30 kbar and 700–900°C gave the samples with lattice parameters varying from 10.174 to 10.202 Å. Metallic–semiconducting transitions were observed for the samples with smaller lattice parameters of 10.174 < a < 10.189 Å\(^{9}\). Attempts to synthesize the pyrochlores with this lattice parameter range were unsuccessful under the reactions in sealed Ag or SiO₂ tubes. Further studies using high pressure synthesis are necessary in order to clarify the metallic–semiconducting transition at 120 K.

Relationship between the structure and electrical properties

Like the cubic–perovskite structure, the pyrochlores A₂B₂O₆O' have BO₃ array of corner shared octahedra, but the B–O–B angles are reduced from 180° to about 130°\(^{9,11}\). Reduction of the B–O–B angles from 180° reduces the B–O–B overlap integrals; the electrical properties of the pyrochlores might thus be affected by a small change in the B–O–B angle.

The structural data using neutron diffraction measurements revealed that the HT phase has smaller Ru–O(1) distance and larger Ru–O(1)–Ru angle, indicating stronger Ru–O–Ru interaction. The O(1)–Ru–O(1) angle, which is an indication of the RuO₆ octahedra distortion, is smaller in the HT phase than in the LT phase. This is consistent with the electrical properties that the HT phase showed metallic and the LT phase showed semiconducting.

Structure and electrical properties of the ruthenate pyrochlores were previously reported for metallic Bi₂Ru₂O₆, and Pb₂Ru₂O₆, semiconducting Y₂Ru₂O₆, and Ln₂Ru₂O₆ (Ln = Pr, Nd, Sm, Dy), and their solid solutions\(^{7,12,13}\). Figure 5 shows the A–O distances, the Ru–O distances, and the Ru–O–Ru angles in the ruthenate pyrochlores as a function of lattice parameters. The A–O(2) distances, which are determined by the lattice parameters, increase with the lattice parameters. Linear relationship is also observed for the A–O(1) and A–O(average) distances in the semiconducting pyrochlores with A = Ln, Y. However, larger A–O distances are observed for the Tl, Pb, and Bi pyrochlores. The interaction between Ru–O(1) and A–O(1) might be competitive; weaker the A–O(1) interaction, stronger the Ru–O(1) interaction. This is consistent with metallic character for the Bi, Pb and Tl(HT) phases. For the Ru–O distances, the semiconducting pyrochlores show longer distances than the metallic pyrochlores. Tl₂Ru₂O₇ (LT) is situated on a borderline between the metallic and
Fig. 4. Resistivity curves for Ti$_2$Ru$_2$O$_{7-\delta}$.

Fig. 5. Bond distances and angles as a function of lattice parameters.
(a) A–O(1) distance; (b) Ru–O(1) distance; (c) Ru–O(1)–Ru angle.
semitransducing regions. The semiconducting pyrochlores show the Ru–O–Ru angles between 129°(Y₂Ru₂O₇) and 134°(Pr₂Ru₂O₇), while the metallic pyrochlores have larger Ru–O–Ru angles of 135°(Tl₂Ru₂O₇₅₋₁) – 140°(Bi₂Ru₂O₇). Smaller Ru–O distances and larger Ru–O–Ru angles lead to the increased overlap between Ru and O, which causes more conducting behavior in the Bi, Pb, and Tl pyrochlores.

In summary, the Ru–O distances of the metallic pyrochlores (A=Bi, Pb, Tl) are 1.94 – 1.95 Å, and those of the semiconducting pyrochlores (A = Ln, Y) are 1.98 – 1.99 Å. The Ru–O–Ru angles of the semiconducting pyrochlores are 129° – 134°, while those of the metallic pyrochlores are 135° – 140°. Metallic property of these pyrochlores is presumed to be associated with the increased overlap as measured by the Ru–O distances and Ru–O–Ru angles.

REFERENCES

NEUTRON SCATTERING STUDIES OF Fe/Cr MULTILAYERS

Hideki YASUDA, Masayasu TAKEDA, Yasuo ENDOH, Kazuyoshi YAMADA, Tsukasa WATANABE, #Atushi KAMIJO and †Junichiro MIZUKI

Department of Physics, Faculty of Science
Tohoku University
Sendai, 980 Japan

#Fundamental Research Labs, NEC Corp.,
4-1-1 Miyazaki, Miyamae-ku,
Kawasaki, 216 Japan

†Fundamental Research Labs, NEC Corp.,
34 Miyukigaoka, Tsukuba, 305 Japan

ABSTRACT

We have performed the off specular neutron scattering measurement in order to elucidate the relation between a giant magnetoresistance effect and the magnetic disorder at the interfaces. Intense off specular diffuse scattering indicating the magnetic disorder at the interfaces was clearly observed, which may cause a giant magnetoresistance effect.

INTRODUCTION

Artificial metallic multilayers show a lot of unique properties. A giant magnetoresistance (GMR) effect is one of the most representative one and has been discovered in Fe/Cr multilayers for the first time. The GMR effect in this multilayer arises when magnetic moments of adjacent Fe layers couple antiferromagnetically through the Cr layer in the absence of magnetic fields. Antiferromagnetic structure of the Fe layers goes to ferromagnetic one in the fields higher than saturation field through a canting state. The resistivity decreases with increasing the magnetic fields until the magnetization saturates. The ratio, \( \Delta R/R \), reaches up to 50%, where \( R = R(H > Hs) \) and \( \Delta R = R(H = 0) - R \). Several theoretical models propose that the origin of the GMR effect is spin-dependent scattering of conduction electrons which is induced by interfacial atomic disorder between the Fe and the Cr layers. The close relation between the GMR effect and the interfacial roughness is supported by some experimental works, which show that the moderate interfacial roughness enhances the GMR effect. However, Takanashi et al. claimed that the bulk scattering of electrons is more important than the interfacial scattering. Atomic interfacial roughness causes the magnetic disorder of Fe moments which has been paid little attention. It is very important for the complete understanding of the GMR effect to investigate the magnetic disorder at the interface as well as atomic interfacial roughness. We have performed neutron scattering measurement of Fe/Cr multilayers in order to elucidate the relation between the GMR effect and the magnetic disorder at the interface.
EXPERIMENT

We prepared two samples by Molecular Beam Epitaxy (MBE). One is $[\text{Fe}(30\text{Å})/\text{Cr}(10\text{Å})]_{80}$ grown epitaxially on an $\text{Al}_2\text{O}_3(1\bar{1}02)$ substrate, on which buffer layers (Nb 2000Å, Cr 750Å) were deposited previously. The suffix number 80 outside of squared column means the total number of bilayers. The other sample is $[\text{Fe}(30\text{Å})/\text{Cr}(10\text{Å})]_{51}$ grown on a MgO(0 0 1) substrate with Cr buffer layer of 1000Å. The thickness of the Fe and Cr layers is designed to obtain the largest GMR effect\(^7\). We define the former sample as "sample-A" and the latter as "sample-B" for convenience.

The magnetization was measured by SQUID magnetometer (Quantum Design MPMSR2) for sample-A and VSM for sample-B, respectively. An external magnetic field was applied in the multilayer plane.

Neutron scattering measurements were carried out by the TOPAN spectrometer installed at JRR-3M at Tokai Establishment of JAERI. The wavelength of an incident neutron was fixed at 2.43Å by pyrolytic graphite monochromator, and higher order reflection was removed by a pyrolytic graphite filter set before a sample. External magnetic fields were applied parallel to the sample plane up to 8.5 (kOe). Two types of measurements have been done. One is the specular scattering measurement ($\theta - 2\theta$ scan), and the other is the off specular diffuse scattering measurement around the Bragg peaks.

RESULTS AND DISCUSSIONS

Figure 1(a) and (b) show the magnetization measurement for the sample-A and sample-B, respectively.

![Graph](image)

Fig.1  The magnetization curve at room temperature for sample-A by SQUID (a) and for sample-B by VSM (b).
The magnetization of sample-A and sample-B saturated at about 7(kOe) and 8.5(kOe). This means that the antiferromagnetic coupling between the magnetic moment of adjacent Fe layers in sample-B is stronger than that in sample-A. The reduction of magnetization in the magnetic fields \( H > 10(\text{kOe}) \) and \( H < -10(\text{kOe}) \) in Fig.1(b) is due to the diamagnetization of the substrate, sample holder and so on.

The specular scattering measurements (\( \theta - 2\theta \) scan) in zero field at room temperature for each sample are shown in Fig.2(a) and (b). Here, we define the parallel and the perpendicular component of the scattering vector to the sample plane as \( q_x \) and \( q_z \), respectively (Fig.3). The \( q_x \) is chosen in arbitrary direction in the sample plane. The peaks at \( q_z = 0.07(\AA^{-1}) \) and \( q_z = 0.13(\AA^{-1}) \) for sample-A are Bragg peaks from the antiferromagnetic structure of Fe layers (\( d = 80\AA \)) and from the bilayer of Fe/Cr (\( d = 40\AA \)), respectively. We define the former Bragg peak as 1/2 Bragg peak and the latter as 1st Bragg peak. The peaks at \( q_z = 0.19(\AA^{-1}) \) and \( q_z = 0.26(\AA^{-1}) \) are the higher order Bragg peaks. The similar peaks are observed for sample-B. The small difference of peak positions between two samples is due to the difference of the bilayer period.

![Fig.2](image)

*Fig.2* The specular scan (\( \theta - 2\theta \) scan) for sample-A (a) and for sample-B (b) in zero field at room temperature.

![Diagram](image)

*Fig.3* \( q_x \) and \( q_z \) indicate the parallel and the perpendicular component of the scattering vector to the sample plane, respectively. The \( q_x \) is chosen in arbitrary direction in the sample plane.
Figure 4(a) and (b) show the field dependence of profile of the off specular scan around the 1/2 and the 1st Bragg peaks for sample-A, respectively. The same scans in various fields for sample-B are also shown in Fig. 5(a) and (b). The off specular scan in the reciprocal space is displayed schematically by the arrows in Fig. 6.

![Image of figure 4](image4.png)

**Fig. 4** The field dependence of diffuse intensities around the 1/2 Bragg point (a) and the 1st Bragg point (b) for sample-A at room temperature.

![Image of figure 5](image5.png)

**Fig. 5** The field dependence of diffuse intensities around the 1/2 Bragg point (a) and the 1st Bragg point (b) for sample-B at room temperature.
The sharp components at \( q_x = 0 \) (Å⁻¹) positions are the Bragg peaks. The decrease of the intensity of the 1/2 Bragg peak by applying the magnetic field is caused by decrease of antiferromagnetic component of Fe layers, and the increase of the 1st Bragg peak intensity comes from the increased ferromagnetic component. Around the 1/2 and 1st Bragg peak for sample-A, intense and broad off specular diffuse scattering is observed at \( H = 0 \) (kOe) and intensities of this scattering decrease as the applied magnetic field is increased. The off specular diffuse scattering around the antiferromagnetic Bragg peak indicates the existence of the magnetic disorder at the interfaces between the Fe and the Cr layers. The atomic disorder at the interfaces is also observed as the off specular diffuse scattering around the 1st Bragg peak which is insensitive to the magnetic fields. On the other hand, intense off specular diffuse scattering appear around neither the 1/2 nor the 1st Bragg peak for sample-B. This means that sample-A has atomic and magnetic rougher interfaces than sample-B.

We have estimated the integrated intensities of the Bragg peak and the off specular diffuse scattering around the 1/2 Bragg peak. A Gaussian and two Lorentzian functions were used for the fitting functions. The Gaussian function corresponds to the specular reflection and two Lorentzian functions correspond to the diffuse component, respectively. One of the Lorentzians expresses the main diffuse scattering, and the other expresses the weak diffuse scattering like background. We have also done a preliminary fit to the data by a theoretical model for the off specular diffuse scattering from the multilayers with rough interfaces. In this model, the off specular diffuse scattering is expressed by a sum of Lorentzian functions.

The both fittings show the same tendency, namely, the integrated intensities of diffuse scattering reduce in proportion to the integrated intensity of the Bragg peak. Recently, it has been reported that the resistivity change, \( R(H) - R(H > H_s) \), was proportional to the intensity of the 1/2 Bragg peak, where \( H_s \) is the saturation field. Therefore, it can be concluded that the resistivity change is also proportional to the magnetic diffuse intensity.

**SUMMARY**

We have observed intense off specular diffuse scattering around the antiferromagnetic Bragg peak which indicate the magnetic disorder at the interfaces in the Fe/Cr multilayers, for the first time. We have found out that the integrated intensity of the diffuse scattering is proportional to the resistivity change by applying magnetic fields. This suggests that the magnetic disorder at the interface plays an important role on the GMR effect.
References:

**P-129**

**Cu ION DISORDERING IN HIGH IONIC CONDUCTOR Rb₄Cu₁₆I₇₋ₓClₓ**

*Hitoshi KAWAJI, *Tooru ATAKE, **Ryoji KANNO, ***Fujio IZUMI and ****Osamu YAMAMOTO

*Research Laboratory of Engineering Materials
Tokyo Institute of Technology
4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 Japan

**Faculty of Science, Kobe University
1-1 Rokkoudai-cho, Nada-ku, Kobe, 657 Japan

***National Institute for Research in Inorganic Materials
1-1 Namiki, Tsukuba, 305 Japan

****Faculty of Engineering, Mie University
1515 Kamihana-cho, Tsu, Mie, 514 Japan

**ABSTRACT**

The properties of a high ionic conductor Rb₄Cu₁₆I₇₋ₓClₓ were studied by neutron and X-ray diffraction, and heat capacity measurements. The structure parameters of Rb₄Cu₁₆I₇₂Cl₂ were obtained by the Rietveld analysis of TOF neutron diffraction data between 50 and 300 K, which showed gradual excitation of migration of Cu ions from Cu(3) site into Cu(2) site with increasing temperature from about 100 K to room temperature. The heat capacity was measured between 10 and 300 K using a high precision adiabatic calorimeter. An abnormal increase was observed in the heat capacity curve above about 100 K. The excess heat capacity showed a broad anomaly with a maximum at about 190 K. The measurements were also made of Rb₄Cu₁₆I₇Cl₁₃ which showed slight different properties from Rb₄Cu₁₆I₇₂Cl₂.

**INTRODUCTION**

Since the discovery of high copper ion conductivity in CuCl-CuI-RbCl system by Takahashi et al.¹, a number of studies have been made in the fields of fundamental science and applications. The sample of Rb₄Cu₁₆I₇Cl₁₃ showed extremely high conductivity of 0.34 S/cm⁻¹ with a low activation energy of 7.0 kJ/mol⁻¹ at room temperature, and a high performance has been expected in the application of the compound to rechargeable solid electrolyte cells²,³. The more detailed studies⁴,⁵ have revealed a narrow solid solution range, and the compound is represented as Rb₄Cu₁₆I₇₋ₓClₓ.

The crystal structure of Rb₄Cu₁₆I₇₋ₓClₓ is the same as that of RbAg₄I₅ at room temperature⁶. Sixteen Cu ions can occupy three kinds of site, Cu(1), Cu(2) and Cu(3); the number of each site is 8, 24 and 24, respectively. In the case of RbAg₄I₅, the ordering of Ag ion takes place at low temperatures associated with structural phase transitions⁶,⁷. A phase transition has been also reported in Rb₄Cu₁₆I₇₋ₓClₓ by electrical conductivity measurements⁴,⁸,⁹, while Geller et al.¹⁰ suspected the existence of phase transition.
Recently, Trukovic and Sokcic\textsuperscript{(1)} proposed a gradual phase transition by DSC measurements. There are serious confusions and/or ambiguities in the previous reports, and the properties and mechanism of the high ionic conductivity of Rb$_4$Cu$_{16}$I$_{7+x}$Cl$_{13-x}$ have not been clarified yet.

In the present paper, the structure parameters obtained by X-ray and neutron diffractometry\textsuperscript{(12)}, and the heat capacities of Rb$_4$Cu$_{16}$I$_7$Cl$_{13}$ and Rb$_4$Cu$_{16}$I$_7$Cl$_{12.8}$\textsuperscript{(13)} are analyzed and the mechanism of Cu ion motion is discussed.

**EXPERIMENTAL**

The samples of Rb$_4$Cu$_{16}$I$_7$Cl$_{13}$ and Rb$_4$Cu$_{16}$I$_7$Cl$_{12.8}$ were prepared by a method of solid state reaction\textsuperscript{(9)} with anhydrous CuCl, CuI and RbCl (99.9% purity) purchased from Nakarai Co. CuCl was purified by recrystallization in hydrochloric acid. The recrystallized CuCl was completely dried at 403 K in a Pyrex tube under vacuum. CuI and RbCl were used after drying in vacuo at 403 K without further purification. The mixture of CuCl, CuI and RbCl was heated under vacuum for 3 h at 403 K to remove water. The sample was ground, pressed into pellets, and then heated for 24 h at 403 K in an evacuated-sealed Pyrex tube. The grinding and heating process was repeated several times, and finally no change in the X-ray diffraction pattern of the product was observed.

X-ray diffraction patterns of the powder samples were obtained between 77 and 473 K. The structure parameters were obtained by Rietveld analysis with the computer program RIETAN\textsuperscript{(14)}.

Neutron diffraction measurements were carried out using the high-resolution TOF neutron powder diffractometer, HRP\textsuperscript{(15)}, at National Laboratory for High Energy Physics. The container of the specimen was a cylindrical vanadium cell (10 mm in diameter and 42 mm in height). The intensity data were acquired at 50, 110, 220 and 300 K.

The heat capacity was measured between 10 and 300 K using the adiabatic calorimeter\textsuperscript{(16,17)}. The amounts of the powdered samples of Rb$_4$Cu$_{16}$I$_7$Cl$_{13}$ and Rb$_4$Cu$_{16}$I$_7$Cl$_{12.8}$ were 13.4394 g (0.00496319 mol) and 14.3005 g (0.00524575 mol), respectively. The contribution of the sample to the total heat capacity was about 70% at 15 K, 40% at 50 K, and 30% above 100 K in the both cases. No abnormal relaxation or hysteresis phenomenon was observed during the experiments.

**RESULTS AND DISCUSSION**

The X-ray diffraction patterns could be indexed on the basis of cubic cell with space group P4$_3$32 or P4$_1$32. No symmetry change was observed during the experiment in the temperature range from 77 to 473 K. The structure parameters were obtained by the Rietveld analysis on the structure reported by Geller et al.\textsuperscript{(10)}. The agreement factor $R_1$ was less than 10% for the data at all the temperatures. Fig. 1 shows the temperature dependence of the lattice constant. A slight change is seen above 150 K, where the anomaly in the electrical conductivity was detected.

The neutron diffraction patterns showed also no significant variation between 50 and 300 K. The refinement of the structure was proceeded with space group P4$_1$32. The site occupancies of Cu ions at the Cu(1), Cu(2) and Cu(3) sites were calculated. The structure became unstable with including the anisotropic thermal vibration. Therefore, at first the occupancies were fixed at the values obtained assuming isotropic thermal vibration, and then the anisotropic thermal parameters were refined. The occupancies at 300 K were determined as to be 0.342(5), 0.287(5) and 0.110 at Cu(1), Cu(2) and Cu(3) sites, respectively. The temperature dependences of the site occupancies are shown in Fig. 2. At 50 K, the occupancies are 0.341(3), 0.260(3) and 0.195, at Cu(1), Cu(2) and Cu(3), respectively. Above about 100
K, the occupancy at Cu(3) site decreases, while that at Cu(2) site increases. The thermal parameters for Cu ion sites increase considerably with increasing temperature, whereas those for Rb, Cl and I increase slightly from about 0.5 Å² at 50 K to 1-2.5 Å² at 300 K. Large increase in the parameters for Cu(1) and Cu(2) sites indicates a gradual excitation of migration of the Cu ions above about 100 K, which might mainly participate in the ionic condition.

The measured molar heat capacities of Rb₄Cu₁₆I₇Cl₁₃ are shown in Fig. 3. The heat capacity curve shows an abnormal increase above about 100 K, and the value exceeds the classical limit value of 120R = 998 JK⁻¹mol⁻¹ above 130 K. To estimate the excess heat capacity, the normal portion of the heat capacity was calculated as follows. The lattice vibrational contribution was calculated by a combination of Debye and Einstein functions fitted to the heat capacity data below 80 K. The correction of \( C_p - C_v \) was made by using the Nernst-Lindemann relation; it is about 4% of \( C_v \) at 300 K. The calculated normal portion is represented by a solid line in Fig. 3. The excess heat capacity obtained by subtracting the normal portion from the measured molar heat capacity is shown in Fig. 4, where a maximum is at about 190 K.

Such a broad anomaly in the heat capacity indicates a noncooperative mechanism for the excitation of migration of Cu ions on the crystal sites, to which Schottky type model or quasi-chemical approximation\(^{11,18,19}\) should be applicable. A well fitted curve of Schottky heat capacity is shown by a solid line in Fig. 4, where 6.62 mol of two level system is assumed with ten times degeneracy of the exited state by

![Fig. 1. Lattice constants of Rb₄Cu₁₆I₇Cl₁₃ (○) determined by X-ray diffraction and Rb₄Cu₁₆I₇.2Cl₁₂.8 (▲) determined by neutron diffraction.](image)

![Fig. 2. Occupancies of Cu ions at Cu(1), Cu(2) and Cu(3) sites of Rb₄Cu₁₆I₇.2Cl₁₂.8 determined by neutron diffraction.](image)
5.7 kJmol\(^{-1}\) above the ground state. A quasi-chemical approximation may be available in this phenomenon. We tried to see the excess heat capacity of Rb\(_4\)Cu\(_{16}I_{17}Cl_{13}\) by applying the same method of quasi-chemical approximation as for disordering of Ag ion in RbAg\(_4I_5\) reported by Wiedersich and Johnston\(^1\)\(^9\). However, the agreement between the experimental heat capacity curve and the calculated one was less satisfactory. The calculated temperature dependences of the occupancies of the three sets of Cu sites were not consistent with the results of neutron diffraction. The calculated occupancy at Cu(1) site decreases with decreasing temperature, while the value obtained by the neutron diffraction increases from 0.111 (at 300 K) to 0.195 (at 50 K) as shown in Fig. 2. The quasi-

---

**Fig. 3.** Molar heat capacity of Rb\(_4\)Cu\(_{16}I_{17}Cl_{13}\). Solid line denotes the normal portion of the heat capacity.

---

**Fig. 4.** Excess heat capacities of Rb\(_4\)Cu\(_{16}I_{17}Cl_{13}\) (○) and Rb\(_4\)Cu\(_{16}I_{7.2}Cl_{12.8}\) (▲). Solid line shows a heat capacity curve fitted to Rb\(_4\)Cu\(_{16}I_{17}Cl_{13}\) by Schottky type model assuming a two level system.
necessary to take account of the temperature dependence of those energies and/or the next-nearest neighbor interactions.

A similar analysis was made by Trukovic and Sokcevic\textsuperscript{11}) for their DSC data of a compound with slightly different composition Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.66}Cl\textsubscript{13.34}. However, their data are quite different from the present results. To examine the possibility that the discrepancy may be caused by a little difference in the composition of the compounds, we measured the heat capacity of Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.2}Cl\textsubscript{12.8}. The excess heat capacities of Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.2}Cl\textsubscript{13} and Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.2}Cl\textsubscript{12.8} are compared in Fig. 4. The excess heat capacity corresponds to the remarkable variation of the occupancy at Cu(1) site as shown by the neutron diffraction. Therefore, the larger excess heat capacity of Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.2}Cl\textsubscript{12.8} implies that the Cu ions should be more mobile in the crystal, which is compatible with the fact that Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7.2}Cl\textsubscript{12.8} has higher ionic conductivity than Rb\textsubscript{4}Cu\textsubscript{16}I\textsubscript{7}Cl\textsubscript{13}\textsuperscript{10}).

REFERENCES

DETERMINATION OF PARAMAGNETIC $\chi(q,\omega)$ FOR A METALLIC ANTIFERROMAGNET Mn$_3$Pt BY TOF METHOD

Yoshiei TODATE, *Keisuke TAJIMA, *Akira YAZAKI, **Shoichi TOMIYOSHI and
†Hironobu IKEDA

Department of Physics, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku,
Tokyo 112 Japan

*Department of Physics, Faculty of Science and Technology, Keio University, Hiyoshi,
Yokohama 223 Japan

**Department of Material Science and Engineering, Faculty of Engineering, Ehime University,
Matsuyama 790 Japan

†National Laboratory for High Energy Physics, Oho, Tsukuba 305 Japan

ABSTRACT

Neutron paramagnetic scattering from a single crystal Mn$_3$Pt which is a Cu$_3$Au type metallic antiferromagnet has been observed by a time-of-flight inelastic spectrometer MAX. Intensity maps along the [100] direction at $T=1.01T_N$ and along [010] at $T=1.01, 1.1, 1.2$ and $1.5T_N$ have been obtained by correcting the instrumental resolution. The results are analyzed by assuming a double Lorentzian form for the scattering function and inverse correlation length $\kappa(T)$, wave vector dependent susceptibility $\chi(q,T)$ and spectral width $\Gamma_3(T)$ are deduced.

INTRODUCTION

In the field of condensed matter physics, time of flight (TOF) neutron spectroscopy with the pulsed spallation sources is a powerful tool of observing the scattering function $S(Q,\omega)$ in wider $q-\omega$ space. However it has been thought that this method is not always suitable for the study of coherent response from single crystal samples. Multi analyser crystal spectrometer (MAX), installed at the pulsed spallation source KENS at KEK, is a unique neutron inelastic spectrometer which enables to observe the collective excitations in single crystals along any crystalloographic direction passing through a particular reciprocal lattice point(1). The remarkable advantage of MAX is, compared to the chopper monochromator spectrometer at the pulsed sources and conventional triple-axis spectrometer at the steady sources, that intensity distribution along the principal axis of the crystal can be mapped out efficiently by fifteen anlyser-detector systems which compose the spectrometer. This unique capability of MAX is especially suited for the observation of an overall feature of the collective excitations, and has already exhibited by determining dispersion relations of phonons and magnons in various materials.
Although the scans made by the detectors of MAX are neither "constant-q" nor "constant-E" because of the TOF method with fixed analyser energy $E_t$, nearly equivalent information will be obtained by interpolation or extraction of the data points so as to obtain the constant-q or -E spectrum. It is therefore essential to normalize the observed intensity of all the time channels by taking the finite instrumental resolution effect into account in order to obtain correct scattering intensity and physical parameters in a model scattering function. Due to the principle of MAX the analyser energy, consequently the resolution, of each analyser-detector system differs significantly from the others. The resolution function for MAX has been derived in a form of conventional four-dimensional Gaussian with a Gaussian approximation for all the elements which give the finite $Q$- and energy-resolution\(^2\). The $Q$- and energy-resolution are highly correlated each other as they are in the triple-axis spectrometer. Being deconvoluted with this resolution function, an intensity map of the scattering function $S(Q,\omega)$ is obtained at the same time from the fifteen TOF spectra.

One of the main purposes of MAX is to observe the higher energy coherent response from magnetic materials. We present here the paramagnetic scattering study of metallic antiferromagnet Mn$_3$Pt. Magnetic scattering from metallic magnets is a typical example which needs information of accurate intensity distribution over wide $q$-$\omega$ space, and spin fluctuations in the paramagnetic state is important for understanding of the strongly correlated electron magnetism. These study has always encountered the experimental difficulties since the wider $q$-$\omega$ region must be surveyed.

**EXPERIMENTAL RESULTS AND ANALYSIS**

Extensive investigations on the paramagnetic response from the metallic magnets have been carried out for various ferromagnets including Fe and Ni. However the study of the metallic antiferromagnets is not sufficient. The response from the metallic antiferromagnets is characterized by the scattering by spin waves with steep dispersion below the Néel temperature($T_N$) and the widely spread paramagnetic scattering above $T_N$. As described above, scattering study of the metallic antiferromagnets over whole temperature range is suited to the MAX-type inelastic spectrometer.

Mn$_3$Pt is an antiferromagnet with the Cu$_3$Au type crystal structure\(^3\). Below $T_N$ (=475K) collinear spin structure is observed. In the collinear structure two Mn atoms in the chemical unit have the magnetic moment of 3.4$\mu_B$ but the other one has no magnetic moment. There is another magnetic transition at $T_1$=365K and the magnetic structure below $T_1$ is a triangular structure with spins perpendicular to (111)-axis. We have already performed and reported spin-wave scattering study of Mn$_3$Pt in both phases\(^4\). The paramagnetic scattering measurements were made on the [100] direction around the ($\frac{1}{2}$10) magnetic Brillouin zone at $T=1.01T_N$ and on the [010] direction around ($\frac{5}{2}$10) at $T=1.01$, 1.1, 1.2 and 1.5$T_N$. The scattering diagram for the [010] direction and the relevant $q$-$\omega$ region covered by the TOF scans are shown in Fig.1.

Neutron scattering cross section is expressed by the scattering function $S(Q,\omega)$ and the scattering function can be expressed in terms of the generalized susceptibility $\chi(Q,\omega)$,

$$\frac{d^2\sigma}{dsd\omega} = N \left( \frac{e^2\gamma}{mc^2} \right) \frac{k_f}{k_i} |f(Q)|^2 S(Q,\omega),$$

(1)

$$S(Q,\omega) = \frac{\pi}{\pi g^2 \mu_B^2} \frac{1}{1 - \exp(-\hbar\omega/\kappa T)} \text{Im} \chi(Q,\omega).$$

(2)
The simplest form of the scattering function for the paramagnets at small $q$-region would be a double Lorentzian,

$$S(q,\omega) = \frac{\chi(0)}{\pi g^2 \mu_B^2} \frac{\pi \omega}{1 - \exp(-\pi \omega/kT)} \frac{\kappa^2}{\kappa^2 + q^2} \frac{\Gamma_q}{\Gamma_q + \omega^2}.$$  \hspace{1cm} (3)

This form has successfully applied to the paramagnetic scattering from various types of magnet. For larger $q$, however, the spectral shape function usually deviates from the Lorentzian.

![Scattering diagram for the [010] measurement (left), and $q$-$\omega$ area (right) covered by the TOF scans made by MAX.](image)

In the analysis of the the paramagnetic scattering measured by MAX, the scattering function is convoluted with the resolution function and fitted to each TOF spectrum by a least square fitting method, and an intensity map is obtained by arranging these "deconvoluted" spectra. Although the result is essentially dependent upon the model scattering function, this intensity map gives correct intensity distribution.

![Fig. 2. Temperature dependence of $\chi(q)$. Intensities are normalized at $q=0$. Lines indicate the fitted Lorentzian.](image)

![Fig. 3. Temperature dependence of $\Gamma_q$. Lines are the fitted function $\Gamma_q = \lambda(1-\cos2\pi\zeta)+\Gamma_0$.](image)
From the mapped scattering intensity for Mn$_3$Pt, the width $\Gamma_q$ of the spectral function $F(q,\omega)$ has been determined from the extracted "constant-q" spectra and the inverse correlation length $\kappa$ has been obtained by the integration of $S(Q,\omega)$ with respect to $\omega$. Temperature variation of $\chi(q)$ and $\Gamma_q$ thus obtained are shown in Figs. 2 and 3 respectively. A functional form for $\Gamma_q$ is assumed to be $\Gamma_q=\Lambda(1-\cos2\pi\xi)+\Gamma_0$ instead of $Aq^2+\Gamma_0$, since the width begins to deviate from the quadratic form at about $q=0.15\AA^{-1}$. Figure 4 is an example of the fitting of the Lorentzian to the observed TOF spectrum. Figures 5 and 6 display the intensity map at $T=1.01T_N$ for the [010] and [100] direction respectively.

![Graph](image)

Fig. 4. Example of the fitted TOF spectrum at $T=1.2T_N$. A peak on the right side is the incoherent elastic one.

![Graph](image)

Fig. 5. Contour maps for the paramagnetic scattering along the [010] direction obtained at $T=1.01T_N$.

![Graph](image)

Fig. 6. Contour map for the [100] direction obtained at $T=1.01T_N$.

**DISCUSSIONS**

Scattering from Heisenberg ferro- or antiferromagnets with localized spins such as EuO or RbMnF$_3$ has been measured throughout the whole Brillouin zone and spin dynamics in such systems is well described by appropriate theoretical models$^6,7)$. However in the metallic
ferromagnetic systems including Fe and Ni, overall interpretation of the experimental results is not satisfactory. General agreement on the paramagnetic scattering from the metallic magnets would be the larger spectral width (scaled by $T_c$) than that in the localized spin systems\(^8\). In Mn$_3$Pt the scaled coefficient in the quadratic relation $A^* (=0.72\text{meV}^2\text{K}^{-1}$ at $T=1.2T_c$) is also apparently larger than that in RbMnP$_3$ (0.12meV$^2$K$^{-1}$ at 1.25$T_c$). Another remarkable feature in this material is the anisotropic paramagnetic scattering. At $T=1.01T_c$, the scattering intensity is significantly different for two directions: [100] and [010] as shown in Fig 5 and 6. It is interesting to investigate the temperature variation of the anisotropy in the paramagnetic scattering. We note that the anisotropic paramagnetic scattering is also seen in a metallic ferromagnet MnP\(^9\).

In conclusion, we have succeeded in observing the paramagnetic scattering form Mn$_3$Pt. Semiquantitative analysis was made and $\kappa(T)$, $\chi(q,T)$ and $\Gamma_q(T)$ have been determined from $S(Q,o)$ derived from the TOF spectra measured by MAX. Basic procedure to map out the scattering intensity distribution has already been established. Further refinements, for instance, improved treatment of the resolution beyond the Gaussian shape approximation, will be made in the near future.

MAXIMUM ENTROPY METHOD FOR NEUTRON POWDER DIFFRACTION DATA

#Shintaro KUMAZAWA and %Christopher J. HOWARD

*Department of Applied Physics, Nagoya University, Chikusa-ku, Nagoya, Japan
#Department of Physics, Tokyo University of Science, Noda, Chiba, Japan
%Australian Nuclear Science & Technology Organisation, Lucas Heights NSW 2234, Australia

ABSTRACT

The Maximum Entropy Method (MEM) is powerful method to restore the accurate electron density distribution from X-ray diffraction data. It deals with electron density which is always positive. In order to analyze neutron diffraction data by the MEM, it is necessary to overcome the difficulty of negative scattering length of some atoms, such as Ti, Mn. In this work, a new approach to solving the negative scattering problem is described. It is based on nuclear densities rather than densities of scattering length, because the nuclear densities are always positive. The new method is successfully applied to analyze the neutron powder data from two polymorphs of TiO₂, i.e. rutile and anatase. The procedure, like its X-ray counterpart, requires no structural model. The nuclear densities of rutile obtained by the present method is compared with the electron density distribution previously obtained by the MEM analysis. In contrast to the electron density distribution, nuclear densities show completely no density between Ti and O nuclei. It is also revealed that both Ti and O nuclear densities are confined within a very limited space. The present analysis provide a good demonstration of complementary nature of neutron and X-ray diffraction.

INTRODUCTION

It has been known for some years that the Maximum Entropy Method (MEM) gives an electron density distribution which is consistent with the given information and least biased with respect to missing information¹. Recently Sakata & Sato (1990)² used the MEM to derive a precise electron density distribution map for silicon. Sakata, Mori, Kumazawa, Takata and Toraya (1991)³ subsequently proposed a new method for analysing X-ray powder data, using profile fits to extract intensities, least squares refinement to determine the scale factor, and applying the MEM. They applied the method to obtain a high quality electron density distribution for
CeO₂. All these works deals with the X-ray diffraction case, in which the structure factor is written as a Fourier transform of electron density in a unit cell.

In the MEM analysis of X-ray diffraction data, the condition, that the electron density is everywhere positive, plays an important role. In the neutron diffraction case, MEM analysis can be applied to give nuclear density maps. Some atoms, such as H, Ti, Mn etc., have negative scattering length for neutron diffraction. In order to extend MEM analysis to neutron diffraction data, the negative scattering length problem must be overcome. In this paper, a new approach to overcoming the problem is described and applied to the case of rutile (TiO₂). The electron and nuclear densities drawn from the MEM analyses of X-ray and neutron powder data are compared in rutile case. The preliminary MEM maps of electron and nuclear densities for anatase (TiO₂) are also shown in this paper. It is often said that neutron and X-ray diffraction are complementary, since they measure nuclear and electron densities, respectively. The results shown in this paper represent good examples of the complementarity of the two techniques.

MEM ANALYSIS FOR NEUTRON DIFFRACTION DATA

The theoretical treatment of the MEM, which will be extended in this paper to tackle the negative scattering problem, has been described in some detail elsewhere. It is reviewed only briefly here. Using following notation:

ρ(r); electron (or nuclear) density at position r,
τ(r); prior density for ρ(r),
λ; Lagrange undetermined multiplier,
N₁; the number of reflections for non-overlapped peaks,
N₂; the number of reflections for overlapped peaks,
F₀obs(k); the observed structure factors for the reflection k,
σ(k); the standard deviation of F₀obs(k),
V; unit cell volume,
Fcal(k); the calculated structure factor which is expressed

Fcal(k)=V∑ρ(r)exp(-2πikr),
(1)

G₀obs(j); the observed combined structure factors for j-th peak,
σ(j); the standard deviation of G₀obs(j),
m(k); multiplicity of reflection k in the j-th overlapped peak,
Gcal(j); the calculated combined structure factor for overlapped reflections which is expressed as

Gcal(j)=[Σm(k)Fcal(k)²/Σm(k)]¹/²,
(2)

the final equation for MEM analysis is written

ρ(r)=exp[lnτ(r)+(Λ/N)(Σ{1/σ²(k)})
x{Fcal(k)-F₀obs(k)}exp(-2πikr)
+Σ{1/σ²(j)Gcal(j)Σm(k)}{Gcal(j)-G₀obs(j)}
xΣm(k)Fcal(k)exp(-2πikr)]
(3)
where $N=N_1+N_2$ and $\Lambda=\lambda F_{\text{cal}}(0)$. As explained in previous work\textsuperscript{4}, the expression (3) for $\rho(\mathbf{r})$ results from maximising entropy subject to a constraint.

In the X-ray diffraction case, the density was evaluated using (3) in an iterative way, making use of (i) an initial prior distribution in which the $Z$ electrons in the unit cell are assumed uniformly distributed through that cell (ii) 0-th order single pixel approximation which is to replace eq. (1) by

$$F_{\text{cal}}(k)=N \Sigma \tau(r) \exp(-2\pi ik \cdot r)$$

thereby removing all reference to $\rho(\mathbf{r})$ on the right hand side of (3), (iii) the constraint that $F_{\text{cal}}(000)=2Z$, and (iv) all the symmetry requirements of the crystal structure.

In the neutron diffraction case, negative scattering lengths, such as those of H, Ti, Mn nuclei, cause a serious problem if one tries to apply the MEM analysis. In order to solve the negative scattering length problem in neutron diffraction case, an extension of the above MEM theory is made in this work. It is possible to demonstrate the new method in the general case, but here the new approach is described in the case of rutile ($\text{TiO}_2$) for the convenience of practical use and clarity. We deal with nuclear densities instead of the densities of scattering length. These are inherently positive. Furthermore the Ti and O atoms will be treated separately. The following values, therefore, can be defined,

$\rho_{\text{Ti}}(\mathbf{r})$: the density of Ti nuclei at $\mathbf{r}$,
$\tau_{\text{Ti}}(\mathbf{r})$: the prior density for $\rho_{\text{Ti}}(\mathbf{r})$,
$S_{\text{Ti}}$: the entropy term of the distribution for Ti atoms.

Corresponding quantities for O atoms are defined by substituting the subscript Ti by O. We express the total entropy of the system by adding the entropies as

$$S = S_{\text{Ti}} + S_0.$$  \hspace{1cm} (4)

Since $\rho_{\text{Ti}}(\mathbf{r})$ and $\rho_0(\mathbf{r})$ are now nuclear densities, they must be weighted by the scattering lengths in the structure factor calculation. So we have

$$F_{\text{cal}}(k)=N \Sigma [\rho_{\text{Ti}}(\mathbf{r})b_{\text{Ti}}+\rho_0(\mathbf{r})b_0] \exp(-2\pi ik \cdot r).$$ \hspace{1cm} (5)

The constraints remain unchanged. From the condition maximizing the entropy subject to constraints, we find two equations

$$\rho_j(\mathbf{r})=\exp(\ln \tau_j(\mathbf{r})+\Lambda/N)b_j(\Sigma \{1/\sigma^2(k)\})$$

$$x(F_{\text{cal}}(k)-F_{\text{obs}}(k)) \exp(-2\pi ik \cdot r)$$

$$+ \Sigma (1/b_j \sigma^2(j)G_{\text{cal}}(j)\Sigma m(k))\{G_{\text{cal}}(j)-G_{\text{obs}}(j)\}$$

$$x\Sigma m(k)F_{\text{cal}}(k) \exp(-2\pi ik \cdot r))$$ \hspace{1cm} (6)

where $j$ represents Ti or O, $N=N_1+N_2$ and $\Lambda=\lambda n_1$, $n_1$ being the number of j nuclei in the unit cell volume. The number of Ti and O nuclei in a unit cell is 2 and 4, respectively. In general $n_1$ can be regarded as the known value as long as the composition of the material (strictly speaking iso-
tope concentration) is known.

The two equations, one for the nuclei of positive scattering length and the other for the nuclei of negative scattering length, are solved by iterating them in a parallel way. Each atom is taken to have uniform density in the initial state, because that corresponds to the maximum entropy state. Using (6) iteratively until the constraints are satisfied, the MEM solution can be obtained. In this method, as in the corresponding X-ray analysis, no structural model is required as is X-ray case.

MEM MAP

Before proceeding to the MEM analysis, integrated intensities were extracted from the neutron diffraction data (from Howard, Sabine & Dickson, 1991)\(^5\) by use of profile fits. The scale factor was obtained in a standard least squares analysis. The phases of the structure factors were assigned as calculated from the known basic structure of rutile.

In the present approach, two Lagrange multipliers must be used. In the present analysis, the same value was used for both. The number of pixels used in the MEM analysis is 64\(\times\)64\(\times\)64 and the results are given in Fig. 1.

**Fig. 1.** The MEM map of the nuclear density distribution of rutile obtained by the present approach. The (a) and (b) show (002) and (110) plane, respectively. The contour range is from 0 to 10 with 1.0 (n/A\(^3\)) intervals for both (a) and (b). Inside the circles of 1.0 (n/A\(^3\)), there are higher densities of Ti and O nuclei but in order to avoid too dense contour lines, contour lines for higher densities are omitted from the figure.
Fig. 1 (a) and (b) are nuclear density distribution of (002) and (110) planes, respectively. It can be seen that there is virtually no nuclear density between atomic sites. If the lower density contours are drawn, such as 0.1 or less, only the bigger circles around Fig 1 (b) are added. This simple density distribution is the expected distribution for nuclei. The results are judged to be reliable, and it is concluded that the method gives satisfactory results. The comparison with X-ray results will be given in the next section.

It is worthwhile to compare the present MEM results with the results of conventional Fourier transformation. For that purpose, the nuclear density of Fig. 1 is converted to a scattering length density distribution, which is shown in Fig. 2 (a). The density maps obtained by the Fourier transformation using the same data are shown in Fig. 2 (b). Evidently, the latter maps are severely affected by the termination effects. There are substantial spurious peaks between atoms due to the truncation effects. In addition to these truncation effects, the nuclei are spread over in a wide range in Fig. 2 (b) as compared with Fig. 2 (a) in which the nuclei are localized in very small regions around the atomic centers. It is concluded that the MEM map is much more reliable than the corresponding Fourier map in the case of rutile.

---

Fig. 2. The density distribution of scattering length for rutile (a) converted from the MEM nuclear densities (Fig. 1 (a)) and (b) that of the conventional Fourier summation. The contour lines are from -16 to 40 with $4 \times 10^{-13} / \text{Å}^3$ intervals. In Fig. 2 (a), the contour lines of inner area of atomic sites are omitted for the same reason mentioned in the caption of Fig. 1.
COMPLEMENTARITY OF X-RAY AND NEUTRON DIFFRACTION

It is often said that the neutron diffraction is complementary to X-ray diffraction. As for the static structure, it is well known that neutron and X-ray diffraction locate nuclei and electrons, respectively. In the field of accurate structure analysis, however, most efforts have concentrated on the joint refinement of X-ray and neutron diffraction data\(^5,7,8\) rather than on comparison of accurate density distribution maps for nuclei and electrons. Since, for rutile, an accurate electron density map derived by the MEM is already available\(^9\), a comparison with that of the nuclear density map derived in the present work is of particular interest.

In Fig. 3, the (110) plane maps of rutile derived by MEM from neutron and X-ray data are compared. The difference are, as expected, very clear. The X-ray MEM map shows a lot of modulation of electron clouds, such as bonding between Ti and O, and skewness of core electrons of oxygen, whereas the neutron MEM map is extremely simple. The distinctive features in the neutron MEM map are the anisotropic thermal vibration of both Ti and O atoms.

![Diagram](image)

**Fig. 3.** The (110) plane MEM maps of rutile (a) for neutron and (b) for X-ray powder diffraction data. The contour lines for (a) from 0 to 160 with 20 (e/Å\(^3\)) intervals, for (b) from 0 to 4 with 0.4(e/Å\(^3\)).
Very recently, the MEM map of anatase (TiO₂) have been derived from X-ray and neutron powder diffraction data, respectively. In anatase case, the crystal structure also have center of symmetry. It is, therefore, no ambiguities of the phase assignment. In Fig. 4, the (100) plane MEM maps for nuclei and electrons are shown in case of anatase. The characteristic differences mentioned above between X-ray and neutron MEM map can be also seen in anatase case again, that is, chemical bonding due to covalency between Ti and O atoms is clearly recognized in X-ray MEM map and only the smearing of nuclei distribution due to thermal vibrations is revealed around atomic sites in neutron MEM map.

**DISCUSSION**

It is possible to calculate temperature factor from the neutron MEM map since the boundaries of Ti and O atoms are very clear. The principle is very simple. The harmonic and anharmonic temperature factors should be calculated from the second and higher order moments of nuclear density distribution. For that purpose, however, a very fine pixel size is needed.

---

**Fig. 4.** The (110) plane MEM maps of anatase for neutron and X-ray powder diffraction data. The contour lines for (a) from 0 to 160 with 20 (\(n/\AA^3\)) intervals, for (b) from 0 to 4 with 0.4 (\(e/\AA^3\)).
since nuclei are confined in a very limited atomic site. For a simple structure like rutile, it is possible to calculate the MEM map for something like 120x120x120 by a super computer. An alternative is to use very fine pixels only around the atomic sites, since most of pixels between atomic site have virtually zero density in the final MEM map, and for those coarse pixels suffice. It may not, therefore, be advisable to reduce the pixel size in a simple manner, because the computing time would be considerably increased.

One of the promising fields to apply MEM analysis by neutron diffraction seems to be in the structure analysis of super ionic conductor, such as AgI etc. It is said that ions in these substances are located at various sites. As long as the phases of structure factors can be assigned correctly, it should be possible to analyse the experimental data to find the nuclei, without introducing any structural model.

CONCLUSION

The nuclear density maps of rutile and anatase are obtained by the MEM analysis. In order to overcome the difficulty of negative scattering length of Ti atom, two equations are derived; one for the nuclei of positive scattering length and the other for those with negative scattering length. These two equations are iterated in parallel. The resulting MEM map shows (i) peak nuclear densities at atomic sites far in excess of those appearing in Fourier map, and (ii) nuclear densities confined in very small regions around the atomic sites. It is possible to calculate atomic positions, harmonic and anharmonic parameters from the MEM nuclear density map.

Most of the computation in this work were done at the Computer Center of Nagoya University which is gratefully acknowledged by the authors. The authors thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes for the use of the HITAC M-680H and S-820/80 computer and Library Program ABCXYZ written by T. Yamada (IMS). This work has been partly supported by a Grant-in Aid for Scientific Research from the Ministry of Education, Science and Culture.

REFERENCES

PHASE EFFECT IN 3-FOLD AND 6-FOLD POTENTIALS OF CH₃ GROUP
ON Q-DEPENDENCE IN NEUTRON SCATTERING

Y. Ozaki

Department of Chemistry
Nagoya Institute of Technology
Showa-ku, Nagoya, 466 Japan

ABSTRACT

The hindered rotational states are studied for the methyl group in potentials with 3-fold and 6-fold symmetries. The localized rotors are used as orientational bases. The intensities of inelastic neutron scattering are calculated as a function of Q. Because of the correlation between proton spins and rotational motion, Q-dependence of the peak A→A' is strongly influenced by the phase in two symmetries of potentials.

INTRODUCTION

In solid phase, the motion of center of mass of a molecule is much restricted. If the molecule has a side group like CH₃, there appears the other degree of freedom, rotation. This motion is also, more or less, hindered by intramolecular or intermolecular interaction. Therefore, the rotational energy \( E_r \) is deviated from the values of free rotation. The values of \( E_r \) have been observed directly in terms of inelastic neutron scattering for many compounds. They extend from 1 \( \mu \)eV to more than 10 meV. Such an extension is based on the variety of strength and symmetry in rotational potential for the methyl group.

When the energy is smaller than 10 \( \% \) of the value in free rotation, namely than roughly 0.1 meV, a few lower parts of energy levels make bundles and form so called "rotational tunneling" levels. Each part corresponds to the levels splitting from one of librational levels. If the observed energy exceeds several meV, it arises from librational motion. There is a marked tendency to make the smaller tunneling energies against the larger energy between librational levels.

In the following sections, at first the rotational potential of a methyl group in solid phase is expressed by first two terms of expansion. Rotational tunneling energy states are produced by solving the eigenvalue problem of the matrix which contains two transfer elements \( a \) and \( b \) in terms of orientational localized model. Next, Q-dependence of the intensity of neutron scattering is calculated as a function of \( a \) and \( b \) using the above rotational states. Finally, the phase effect in the potential between 3-fold and 6-fold terms on Q-dependence is discussed.
ROTATIONAL POTENTIAL

The hindered rotation is described as the rotational motion of a single particle in the field from several interactions. As a first step, the rotational potential can be expanded in the form of $\Sigma_n (V_n/2) \cos(n \alpha + \alpha_0)$ (n=3m, m=1,2,3,...) due to the molecular symmetry C_3, of a methyl group. Next, if the intramolecular or intermolecular interaction is regarded as significant, some terms in the above expansion may disappear because of the symmetry of space part for the remaining of one molecule or the surrounding crystal lattice. The barrier height $V_0$ and the phase shift $\alpha_0$ in the rotational angle $\alpha$ should be consistent with the experimental result. In most cases, the first two terms (n=3 and 6) of the expansion are employed to elucidate the experimental result. Thus, the rotational potential is expressed as

$$V(\alpha) = \frac{V_3}{2} \cos(3\alpha) + \frac{V_6}{2} \cos(6\alpha + \alpha_0),$$  \hspace{1cm} (1)

where we make $\alpha_0 = 0$.

ROTATIONAL STATES

The rotational tunneling states are formed using the extremely localized orientational bases. When the rotor is around the bottom of the 3-fold potential with quite high barrier, three equivalent orientations are fairly good approximation to the bases of rotational states. Similarly, in 6-fold potential, we may take, as bases, six equivalent orientations which can shift by $\alpha = 60^\circ$ each other. If both 3-fold and 6-fold potentials mix, the whole potential is depicted for example in Fig.1. The bases consisting of two sets with three members are available in this case as shown in Fig.2.

Fig.1 Example of potential with 3-fold and 6-fold symmetries. We fix the ratio of barrier height as $V_3/V_6 = 2.0$ and the phase as $\alpha_0 = 28^\circ$.

![Fig.1 Example of potential with 3-fold and 6-fold symmetries.](image)

Fig.2 Localized orientational bases. They are divided into two sets: $(\phi_1, \phi_2, \phi_3)$ and $(\phi_4, \phi_5, \phi_6)$. Three members in the set can shift by $120^\circ$ each other.

![Fig.2 Localized orientational bases.](image)
Fig.3 Energy levels of the rotor in 3-fold and 6-fold potential. In the high value of p, two librational levels split into two. (b/a=0.6)

It is necessary two sorts of transfer matrix elements a and b to represent the transitions to the neighbours through two angles $\alpha_0$ and $120^\circ - \alpha_0$. The matrix relating to rotational motion in the mixed two types of potential can be constructed using a, b and p which is the energy gap between two sets in bases. The symmetry of system consulted here is reflected directly on this matrix. By solving the eigenvalue problem of the above matrix, we get rotational energy levels as Indicated in Fig.3. There are two librational levels for larger p. Each level splits into two tunneling levels. From the bottom, we call four levels A,E,E',A'. The symbol E or E' stands for doubly degenerated level.

Q-DEPENDENCE OF NEUTRON SCATTERING

From the eigenstates above obtained, the intensity of Inelastic neutron scattering by the methyl group is computed by

$$S(Q,\omega)=\sum p_i(T)\langle f|\sum S_j \exp(iQ.r_j)|i\rangle|^2 \delta(\omega+E_i-E_f).$$  \hspace{0.8cm} (2)

Here, $|i\rangle$ and $|f\rangle$ are the initial and final eigenstates which comprise both rotational part and spin part. The rotational factor $\exp(iQ.r_j)$ is associated with the spin operator $S_j$ because the rotation of a group of three protons in CH₃ correlates highly with nuclear spins. For the small tunneling levels, it is permitted that the thermal population $p_i(T)$ is replaced with the highest temperature limit $p_i(\infty)$. In polycrystalline state, the intensity is formulated as a function of only the size of Q. In Fig.4, the intensities of the allowed inelastic four peaks are plotted versus Q. (1:A->E,E'->A', 2:E->E', 3:A->E',E->A', 4:A->A')

Fig.4 Scattering law of the rotor in 3-fold and 6-fold potential as a function of QR. R is the H-H distance in CH₃. (p=1.0, b/a=0.6)
Fig. 5 Scattering law as in Fig. 4. The phase in the potential is $\phi_s = 60^\circ$.
($p = 1.0$, $b/a = 1.0$)

PHASE EFFECT IN POTENTIAL

Recently, we have calculated Q-dependence of neutron scattering of the methyl group in the case that the potential contains both 3-fold and 6-fold components in the same way. As a result, it appears that the maximum in the intensity of neutron scattering does not shift so much by adding the 6-fold term to the 3-fold term. It is concluded eventually that the obtained Q-dependence does not fit with the observed result of the system accompanied by inelastic four peaks.

In the previous computation, the phase in the potential is restricted with the case of $\phi = \pi/3 (\phi_s = 0)$. Fig. 5 gives the similar situation as in that case. From the experimental point of view, the phase shift $\phi_s$ has the quite important role as shown in other many systems. Therefore, this time we take into account the phase effect in two types of potentials. The transfer of the maximum in Q-dependence will be expected. However, it is not clear that the influence of the phase on the shift of maximum value. The difference obviously turns up in the peak 4: A → A'. It can be presumed that the decrease of $S(Q, \omega)$ in this peak is due to the less correlation between rotation and spin of protons.

The rotational bases employed here might be so simplified. The more realistic model is used to calculate the intensity in solely 3-fold potential. If the better bases are applied to the system with 3-fold and 6-fold potential, the relation between the phase shift $\phi_s$ and the ratio $b/a$ is revealed. The detailed behavior of the Q-dependence could be offered.

ACKNOWLEDGMENTS

The author is indebted to Dr. M. Prager for his pointing out of the significance about the phase effect in potential.

REFERENCES

ANHARMONIC THERMAL VIBRATIONS OF BE METAL FOUND IN THE MEM NUCLEAR DENSITY MAP

Masaki TAKATA, Makoto SAKATA, *Finn K. LARSEN, \$Shintaro KUMAZAWA and \$Bo B. IVERSEN

Dept. of Applied Physics, Nagoya Univ., Nagoya, 464-01 JAPAN
Dept. of Chemistry, Aarhus Univ., DK-8000, Aarhus C, DENMARK
Dept. of Physics, Science Univ. of Tokyo, Noda, Chiba 278, JAPAN

ABSTRACT

A direct observation of the thermal vibrations of Be metal was performed by the Maximum Entropy Method (MEM) using neutron single crystal data. In the previous study, the existence of the small but significant cubic anharmonicity of Be has been found by the conventional least squares refinement of the observed structure factors [Larsen, Lehmann & Merisalo(1980) Acta Cryst. A36, 159-163]. In the present study, the same data were used for the MEM analysis, which are comprised of 48 reflections up to $\sin \theta / \lambda = 1.41 \AA^{-1}$ in order to obtain the high resolution nuclear density of Be without using any thermal vibrational model. It was directly visible in the MEM map that not only the cubic terms but also quartic anharmonicities exist in the thermal vibrations of Be nuclei. In order to evaluate thermal parameters of Be including anharmonic terms quantitatively, the least squares refinement of the effective one-particle potential (OPP) parameters up to quartic term was carried out by using the MEM nuclear densities around atomic sites as the data set to be fitted. It was found that the present treatment has a great advantage to decide the most appropriate model of OPP by visually comparing the model with MEM density map. As a result of the least squares refinement, the anharmonic thermal parameters are obtained as $\alpha_{33} = -0.340(5)[\text{eV/Å}^3]$, $\alpha_{40} = 0$, $\beta_{20} = 9.89(1)[\text{eV/Å}^4]$ and $\gamma_{00} = 0$. No other anharmonic term was significant.

INTRODUCTION

The Maximum Entropy Method (MEM) yields a high resolution electron or nuclear density distribution from even a limited number of diffraction data without using a structural model. Since X-rays are diffracted by electrons, the MEM analysis provides us with the electron density distribution from X-ray diffraction data. Recently, the direct investigations of the real space electronic structure by the MEM have been performed for several substances\(^1\)-7) in order to reveal the bonding nature of the crystalline materials.
Neutrons are scattered from the materials by the interaction with nuclei and magnetic potentials. When the MEM is applied to neutron diffraction data of a non-magnetic substance, the nuclear density distribution is directly produced, which corresponds to spatial smearing of the point nuclei due to the potential in the crystalline field. It is, in principle, possible to study thermal vibrations of crystalline materials directly in the real space without using a model by the MEM.

A conventional approach to describe the atomic thermal vibrations is to determine the parameters of an assumed effective one-particle potential (OPP) which is expanded according to the atomic site symmetry. Thus, the corresponding atomic thermal smearing function (TSF) and the Debye-Waller factor (DFW) can be formalized in terms of the OPP model. In order to determine the potential parameters, X-ray or neutron structure factors are used to be fitted to the calculated values. By using the nuclear densities produced by the MEM, which should be equivalent to the TSF, the thermal parameters of OPP can be determined by fitting MEM densities to densities calculated from OPP. This approach provides an alternative for the determination of thermal parameters. In this work, such an analysis was done for the first time in the case of Be. For this purpose, it has an essential advantage to use a neutron diffraction data, since the thermal vibrations are well defined for nuclei.

It is well known that the Be metal is one of the most hard materials. Larsen, Lehmann and Merisalo (1980) have determined mean-square atomic displacements and antisymmetric atomic vibrations in Be by the conventional analysis by using a neutron diffraction data collected at room temperature with short wave length neutrons, which showed only modest extinction effects. They claimed that Be has a small but significant cubic anharmonic component of the thermal motion even at room temperature, although it is a very hard material. The interest of this study is focused on whether the MEM analysis could also reveal the existence of anharmonic thermal motion of Be, of which contribution is not so big.

THE MEM ANALYSIS

In the present study, the lower angle 48 reflections up to \( \sin \theta / \lambda < 1.41 \text{[Å]}^{-1} \) are used for MEM analysis. The details of the procedure to obtain MEM density distributions are given in Sakata and Sato (1990). The present theory of MEM is based on Collins's formalism. The MEM analysis was carried out by the computer program called MEEP. In the present analysis, the unit cell was divided into 120 X 120 X 120 pixels in order to get good spatial resolution. Hence, one pixel become 0.019[Å] X 0.019[Å] X 0.030[Å]. The total computing time was 727 seconds for 10892 iterations by FACOM VP2600 vector computer.

THE MEM NUCLEAR DENSITY OF BE

The MEM nuclear density distribution of Be in the (110) plane and in the basal plane of hcp structure are shown in Fig.1(a) and (b), respectively. In these figures, the contour lines are drawn in logarithmic scale. At a first glance, it is understood that the nuclear densities of MEM map is concentrated in a small region around the atomic sites. The nuclear density at the peak maxima is 144.772 X 10^{-14}[m/Å^{-3}]. In the interatomic region,
the nuclear density is very close to zero. These features are very reasona-
ble as a nuclear density distribution.

For Be, the MEM electron density distribution based on the X-ray
powder data has been reported by Takata, Kubota & Sakata (1993). In order
to compare nuclear and electron densities of Be, the MEM electron density

Fig.1. The MEM nuclear density distributions of Be at room temperature. (a)
and (b) show maps on the (110) and basal planes, respectively. The contour
lines are on a logarithmic scale with 0.05 X 10^8 (n = 0, 1, 2, ..... ) ( X10^{-14} m/A^2).
The tetrahedral and octahedral holes are marked T and O, respec-
tively.
distribution is shown in Fig. 2 for the same planes as in Fig. 1. The contour lines are drawn only for the lower density region in linear scale to show a modulation of electron clouds. The nuclear densities are confined in a very limited region around atomic site and the peak shape of the atomic site is very sharp, whereas the electron densities are distributed somewhat diffusively as an nature of electrons. Furthermore, the surplus electron densities localized around the tetrahedral voids are clearly visible in Fig. 2, which have been believed to be a kind of the bonding electrons of Be. The MEM nuclear density, on the other hand, has no such a surplus density in the tetrahedral voids. This is an experimental confirmation that the surplus electron densities in the tetrahedral voids are purely due to an electronic origin and represent a kind of chemical bonding of Be metal.

THE ANHARMONIC THERMAL VIBRATIONS OF BE METAL

The nuclear densities in Fig. 1 show characteristic features deformed from the oblate expected from harmonic thermal vibrations, which indicate the existence of anharmonicities of Be thermal vibrations.

In the basal plane, somewhat triangular distribution of nuclear densities is clearly recognized. According to the OPP-model of the thermal vibrations, the characteristic feature of nuclear density due to 3rd order anharmonic motion ought to appear in the basal plane for the hcp structure. Due to 3rd order anharmonic term the effective OPP will be distorted antisymmetrically and the equipotential contours are deformed into a triangular shape\(^7\),\(^1\)\(^2\) in the same manner as in Fig. 1(b). The nuclear densities of basal plane must be influenced by 3rd order anharmonicity, which was discussed in the previous studies\(^9\),\(^1\)\(^3\).

From a study of 4th order anharmonic motion in Zn\(^1\)\(^4\), it is known in what way the nuclear densities deform when the contribution of 4th order anharmonic term in the OPP-model is significant. In Fig. 1 (a), the Be MEM nuclear density shows significant deviations from the elliptical shape of harmonic vibrations. This deformation can be interpreted due to a quartic anharmonic term of the OPP function.

DIRECT FITTING OF MEM NUCLEAR DENSITY BY THE OPP MODEL

The MEM nuclear density shows a direct picture of the atomic thermal displacements and is not impaired by a particular electronic structure caused by, e. g. chemical bonding in a crystal. The obtained MEM nuclear densities, therefore, could be regarded as the TSF which is also known as the probability density function (p.d.f.) of Be. In a simple case like symmetric harmonic vibration, the mean-square atomic displacement can be derived directly from the half width at half maximum of the p.d.f.\(^1\)\(^5\). The present case is not as simple as harmonic but it should be possible to evaluate the potential parameters of OPP, which describe the thermal atomic displacements of the point nuclei, by analyzing the shape of the nuclear density distribution. In this study, the potential parameters of an effective OPP for Be is determined for the first time by 3-dimensional function fitting to the real space MEM nuclear densities. In the OPP model, the anharmonic terms up to 4th order are considered.
Fig. 2. The MEM electron density distributions of Be at room temperature based on X-ray powder diffraction data. (a) and (b) are the (110) and basal planes, respectively. The contour lines are drawn from 0.0 to 2.0 with intervals of 0.05(e/A^3) on a linear scale. The tetrahedral and octahedral holes are marked T and O, respectively.
The OPP model used in the present work is written as

\[
V(u) = \beta_1 (u_1^2 + u_2^2) + \beta_2 u_3^2 \\
+ a_{40} (u_2^2 - 3u_1 u_3^2) \\
+ a_{50}/(3u_1^4 + 3u_2^4 + 8u_3^4 + 6u_1^2 u_2^2 - 24u_1^2 u_3^2 - 24u_2^2 u_3^2) \\
+ \beta_{20}/2(-u_1^2 - u_2^2 + 6u_3^2 - 2u_1 u_2 u_3) \\
+ \gamma_{50} (u_1^2 + u_2^2 + u_3^2 + 2u_1 u_2 u_3 + 2u_1 u_3^2 + 2u_2 u_3^2) \tag{1}
\]

where \(u_1 = \langle 210 \rangle\), \(u_2 = \langle 010 \rangle\) and \(u_3 = \langle 001 \rangle\) are the Cartesian components of the atomic displacement. In equation (1), \(\beta_1\) and \(\beta_2\) are the harmonic parameters, and \(a_{40}, \beta_{20}\) and \(\gamma_{50}\) are the anharmonic (third and fourth order) parameters. Then, the p.d.f., \(P(u_1, u_2, u_3)\), becomes

\[
P(u_1, u_2, u_3) = N \cdot \exp\{-V(u_1, u_2, u_3)/k_B T\} \tag{2}
\]

where \(N\) is the normalization factor.

In the conventional method, it is absolutely necessary to calculate the temperature factor by perform a Fourier transformation of p.d.f. to be included in the structure factor expression. In this process, an approximation is usually introduced such as Taylor expansion of the exponential term, \(\exp[-V(u)/k_B T]\). In the present method, the potential parameters can be determined by a direct least-squares fitting of the MEM densities with p.d.f. without using any approximation for OPP.

**FITTING RESULTS OF THE MEM MAP**

The least-squares fitting was carried out as increasing anharmonic terms. In the equation (1), there are three kinds of anharmonic parameters for the 4th order anharmonic vibration. First two terms, \(a_{40}\) and \(\beta_{20}\), are for anisotropic anharmonic vibrations and last one, \(\gamma_{50}\), is for isotropic one. As for 4th order parameters, the potential model with individual 4th order parameters are examined as well as with all combinations of the three 4th order parameters. Whenever any 4th order parameter is refined, the harmonic and third order anharmonic parameters are always included in the potential model. The values of the cubic anharmonic parameters \(a_{33}\) and \(R\)-factors, defined as \(\Sigma |\rho_{\text{MEM}}(u) - \rho_{\text{cal}}(u)|^2/\Sigma |\rho_{\text{MEM}}(u)|^2\) for the nuclear density, for each of the model did not differ significantly. The R-values were dropped to the order of 2% by introducing any 4th order anharmonic term.

It was very difficult to decide which 4th order anharmonic model is most appropriate only from R-factor. Any 4th order model did not change significantly the nuclear densities on basal plane. The nuclear densities on (110) plane shows considerable difference depending on the potential model. With the visual aid of (110) plane densities, it was concluded that the \(\beta_{20}\) parameter is the most significant and important among 4th order anharmonic parameters. The final values for all the parameters of the present refinement are listed in Table 1. The calculated nuclear density
from OPP model using the final parameters are shown in Fig.3. In the figure, the MEM nuclear densities are well reproduced for both basal and (110) plane.

From Fig.1 (b), it can be easily and visually concluded that due to cubic anharmonic term the potential is softened in the +[210] direction and hardened in the opposite direction. This is consistent with the previous result⁹ and similar to that for the other hcp metals, Mg¹⁶ and Zn²,¹⁷).

---

**Fig.3.** The nuclear densities calculated with the final parameters obtained by the direct fitting with the effective OPP model up to 4th order anharmonic term for sections (a) (110) and (b) basal plane.
This corresponds to a negative sign of $\alpha_{33}$ as listed in Table 2. The value of $\alpha_{33} = -0.340(5)$, show slight different value from the previous result, $-1.00(3)$. This seemed to be caused by exclusion of fourth order term from the potential model in the previous analysis. Thus, the discrepancy between these two values is of no importance.

**Table 1** Final values of potential parameters for Be.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_1$ (eV/$A^2$)</td>
<td>2.7902(5)</td>
</tr>
<tr>
<td>$\beta_2$ (eV/$A^2$)</td>
<td>2.7763(8)</td>
</tr>
<tr>
<td>$\alpha_{33}$ (eV/$A^4$)</td>
<td>-0.340(5)</td>
</tr>
<tr>
<td>$\alpha_{40}$ (eV/$A^4$)</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_{20}$ (eV/$A^4$)</td>
<td>9.89(1)</td>
</tr>
<tr>
<td>$\tau_{00}$ (eV/$A^4$)</td>
<td>0</td>
</tr>
<tr>
<td>$R(\rho^2)$</td>
<td>0.024</td>
</tr>
</tbody>
</table>

The authors thank Prof. J. Danielsen of his kind help with the computation. The authors also thank Prof.s J. Harada and S. E. Rasmussen for their encouragement. Most of the computations were carried out at the Computer Centre of Nagoya University, which is gratefully acknowledged by the authors. The authors thank the Computer Centre, Department of Chemistry, Aarhus University for the use of the workstations. Personal DECstation5000 and IRIS INDIKO. This work has been partly supported by a Grant in Aid of Scientific Research from the Ministry of Education, Science and Culture of Japan and the Danish National Science Research Council.

**REFERENCES**

NEUTRON SCATTERING STUDY OF MnX₂ (X = Br, I)

Taku SATO and Hiroaki KADOWAKI
Department of Physics, Tokyo Institute of Technology
Oh-okayama, Meguro-ku, Tokyo 152, Japan
*The Institute for Solid State Physics, The University of Tokyo
Roppongi, Minato-ku, Tokyo 106, Japan

Abstract

Successive magnetic phase transitions in MnX₂ (X = Br, I), found by bulk measurements, are studied by neutron scattering experiments. There occur two (T₁₁ = 2.32K, T₁₂ = 2.17K) and three (T₁₁ = 3.95K, T₁₂ = 3.8K, T₁₃ = 3.45K) phase transitions in MnBr₂ and MnI₂, respectively. We have found that magnetic structures of the both compounds in the intermediate temperature phases (MnBr₂: T₁₁ > T > T₁₂; MnI₂: T₁₁ > T > T₁₃) are transverse sinusoidally-modulated structures with incommensurate wave-vectors which vary as a function of temperature. As the temperature is lowered into the lowest temperature phases, the magnetic structures change via first order transition into ↑↑↓ and a helical structure for MnBr₂ and MnI₂, respectively, which were determined by previous experiments. The successive phase transitions in MnBr₂ are accounted for quantitatively using a mean field approximation of a Hamiltonian consisting of exchange interactions up to third inter- and third intra-layer neighbor sites and the dipolar interaction.

INTRODUCTION

Magnetic properties of transition metal dihalides which crystallize in CdI₂ or CdCl₂ hexagonal layer structure have been investigated for decades. A spin structure which is most commonly seen in these magnets are the antiferromagnetic stacking of the layers of ferromagnetically aligned spins, which is observed in most of Fe, Co and Ni chlorides and bromides. Among those compounds, MnX₂ (X = Br, I) exhibit complicated structures\(^1,2\). In MnBr₂ magnetic moments order in up-up-down-down sequence with modulation vector \(\vec{q} = (1/4, 0, 1/4)\), where the spin direction is parallel to the b-axis. On the other hand in MnI₂, a proper helical structure with a modulation vector \(\vec{q} = (3/16, 0, 7/16)\) is realized. The complicated structures in MnX₂ are attributed to competing exchange interactions. Recently, two successive phase transitions were found by magnetic circular dichroism\(^3\) and optical birefringence\(^4\) measurements for MnBr₂ and MnI₂, respectively. They showed that the higher and lower temperature phase transitions are a second and first-order transitions, respectively. On a theoretical basis these first-order phase transition is puzzling and cannot be accounted for by a simple Heisenberg model. Since magnetic ions form a Bravais lattice and have Heisenberg spins, the ground state
magnetic structure is a helical structure with a wave vector at which $J(\vec{q})$ has the maximum. If the anisotropy is a pure Heisenberg or an $XY$ type, there occurs only one second-order phase transition in finite temperatures. On the other hand, if the anisotropy is a weak Ising type, two second-order phase transitions take place, where the easy and hard axis components order at a higher and lower temperatures, respectively. Therefore a certain reason other than the weak Ising anisotropy is required for explaining the first-order phase transitions. In this work we have determined magnetic structures in the intermediate phases of Mn$X_2$ by neutron scattering experiments. Using the observed structures we discuss the successive phase transitions on the basis of a mean field approximation.

**EXPERIMENTAL RESULTS**

The single crystals were grown in silica ampoules by the Bridgeman method. Neutron scattering measurements were performed on ISSP-ND1 (JRR-2), 4G-TAS and PONTA (JRR-3M) triple axis spectrometers at JAERI (Tokai). Single crystals of MnBr$_2$ (0.23cc) and MnI$_2$ (0.51cc) were mounted in a $^3$He cryostat. The temperature of the sample was monitored by a Ge sensor and controlled within ±0.01K.

MnBr$_2$

We confirmed that two successive phase transitions occur at $T_{N1} = 2.32$K and $T_{N2} = 2.17$K. Magnetic reflections in the low temperature phase ($T < T_{N1}$) appear at $\vec{q} = \vec{G} \pm \vec{q}$, where $\vec{G}$ and $\vec{q} = (1/4, 0, 1/4)$ denote reciprocal lattice and modulation vectors, respectively. In the intermediate temperature phase ($T_{N1} > T > T_{N2}$), we found that the modulation vector $\vec{q} = \vec{q}_{INC} = (q_*^*, 0, q_*^*)$ becomes incommensurate and depends slightly on temperature. In Fig. 1 we show the magnetic Bragg positions in the reciprocal lattice space and the temperature dependence of the modulation vector $\vec{q}$. It should be remarked that modulation vector exhibits hysteresis effect in the intermediate temperature phase. In Fig. 2 scattering intensities of the magnetic reflections are plotted as a function of temperature. One can see from this figure that $T_{N2}$ is a first order phase transition temperature. Magnetic structures of the low and intermediate temperature phases were determined by observing integrated intensities of the magnetic reflections. We confirmed the previous result that in the low temperature phase, moments order in up-up-down-down-down sequence with modulation vector $\vec{q} = (1/4, 0, 1/4)$, which is shown in Fig. 3.

In the intermediate temperature phase, we found that the transverse sinusoidally-modulated structure is realized. The moments on the $ac$-plane are depicted in Fig. 4.
Figure 1: (a) Nuclear and magnetic Bragg positions in the (h0l) zone of MnBr$_2$. Square denotes nuclear Bragg position. Open and filled circles stand for magnetic Bragg positions at $T_{N1} > T > T_{N2}$ and $T < T_{N2}$, respectively. Inset shows locus of magnetic reflection $\mathbf{Q} \sim (0.38, 0, 0.21)$ which varies as a function of temperature at $T_{N1} > T > T_{N2}$. (b) Temperature variation of modulation vector along the locus. Parameter $\zeta$ is defined in the inset of (a).

Figure 2: (a) Temperature dependence of peak intensity of magnetic reflection in wide (a) and small (b) temperature range. Solid and dashed lines are guides to the eye.
Figure 3: Spin arrangement in the low temperature phase of MnBr$_2$. (a) moments are depicted on the CdI$_2$ structure. (b) moments in the $ac$-plane. Open and filled circles denote up and down spins, respectively.

Figure 4: Spin arrangement in the intermediate temperature phase of MnBr$_2$. The same manner as in Fig. 3 (b) is used to show the moments in the $ac$-plane. Radius of each circle represents magnitude of moment parallel to the $b$-axis.
A new phase transition was found at $T_{N2} = 3.8K$ in addition to the two previously observed transitions at $T_{N1} = 3.95K$ and $T_{N3} = 3.45K$. As temperature is decreased from the paramagnetic phase, magnetic reflections with wave vector $\vec{Q} = \vec{G} \pm \vec{q}$, where $\vec{q} = (0.1025, 0.1025, 1/2)$ appear at $T_{N1}$. The second phase transition temperature $T_{N2}$ is characterized as a temperature below which the modulation vector $\vec{q}$ starts to vary as a function of temperature. The locus of modulation vector is schematically shown in Fig. 5 (a) and (b). At the third phase transition $T_{N3}$ the modulation vector $\vec{q}$ jumps into the $(h 0 l)$ plane at $\vec{q} \approx (0.181, 0, 0.439)$, which is close to the previously reported $\vec{q} = (3/16, 0, 7/16)$, but is definitely incommensurate and exhibits slight temperature dependence. Temperature dependence of the magnetic scattering intensities are shown in Fig.6.

Magnetic structures were determined by observing integrated intensities of magnetic reflections. The helical structure reported in the previous work was confirmed in the low temperature phase ($T_{N3} > T$). In the intermediate temperature phase ($T_{N1} > T > T_{N3}$), the transverse sinusoidally-modulated structure was found. It can be written as $<S_i> = \vec{S} \sin(\vec{q} \cdot \vec{r}_i + \phi)$, where the polarization $\vec{S}$ is in the $c$-plane and perpendicular to the modulation vector $\vec{q}$.

---

Figure 5: (a) Schematic locus of modulation vector $\vec{q}$. $q_1$ and $q_3$ are confined in $(h h l)$ and $(h 0 l)$ planes, respectively. (b) Temperature dependence of $\vec{q} = \vec{q}_2$ is plotted using $\zeta$-axis defined in (a). $\zeta = 0$ corresponds to $\vec{q} = \vec{q}_1$. 

---

- 395 -
DISCUSSION

Present neutron scattering experiment shows that the first order phase transitions in both MnBr$_2$ and MnI$_2$ are characterized by the jumps of the modulation vectors, and that in the intermediate temperature phase the magnetic structures are transverse sinusoidally modulated structures. One can easily attribute the sinusoidally modulated structure to Ising type anisotropies. However the first order phase transitions are puzzling as discussed in the introduction. We attempted to interpret the first order transitions in terms of a model Hamiltonian consisting of the exchange and the dipolar interaction within a mean field approximation.

The model Hamiltonian is given by

$$ H = -2 \sum_{<i,j>} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_{<i,j>} D_{ij}^{\alpha \beta} \vec{S}_i^{\alpha} \vec{S}_j^{\beta} = \sum_{q \neq 0} \vec{S}_q^{\alpha} \vec{S}_q^{\beta} H^{\alpha \beta}(\vec{q}), $$

$$ H^{\alpha \beta}(\vec{q}) = [-J(\vec{q}) \delta^{\alpha \beta} + D^{\alpha \beta}(\vec{q})] \quad (\alpha, \beta = x, y, z), $$

where $D_{ij}^{\alpha \beta}$ and $D^{\alpha \beta}(\vec{q})$ represent the dipolar interaction and its Fourier transform, respectively. Within a mean field approximation, the phase that has the highest ordering temperature corresponds to the lowest eigenvalue of the matrix of $H^{\alpha \beta}(\vec{q})$. To reproduce the sinusoidally modulated structure of MnBr$_2$, we solved the eigenvalue problem including a lot of adjustable exchange constants and found that three intra- and three inter-layer interactions are indispensable for maximizing $J(\vec{q})$ at observed $\vec{q}_{INC}$. The dipolar interaction gives the correct polarization parallel to the b-axis.

At lower temperatures, either the helical with $\vec{q} = \vec{q}_{INC}$ or the up-up-down-down structure is more favorable, since these structures allow greater average moments. Using the parameters which is determined to reproduce the sinusoidally modulated phase, we calculated the free energies of the three structures; (1) incommensurate sinusoidally modulated structure ($F_{ICS}$); (2) commensurate sinusoidally modulated (up-up-down-down)
structure ($F_{CS}$); (3) incommensurate helical structure ($F_{IH}$). They are plotted in Fig. 7. One can see from this figure that the up-up-down-down structure is most stable below $T_{N2}$ and that the transition is first order.

![Graph showing free energies](image)

**Figure 7:** Free energies of incommensurate sinusoidal ($F_{ICS}$), commensurate sinusoidal ($F_{CS}$) and incommensurate helical ($F_{IH}$) structures.

Temperature dependence of the modulation vector in the intermediate temperature phase of MnBr$_2$ were studied. We found that it can be understood quantitatively by using the Landau like expansion of free energy up to 4th order terms. This mechanism is essentially the same as that in the ANNNI model$^7$.

Although the phase transitions in MnBr$_2$ can be understood quantitatively, these in MnI$_2$ are more complex and left for a further study.

**ACKNOWLEDGMENTS**

The authors would like to thank Dr. K. Iio for helpful discussion and Dr. H. Tanaka for permission to use the single crystal of MnBr$_2$.

**REFERENCES**


PRESSURE DEPENDENCE OF THE ANTFERROMAGNETIC ORDERING TEMPERATURE OF FACE-CENTERED-CUBIC IRON

*Akifumi ONODERA, *Yorihioko TSUNODA, *Nobuhiko KUNITOMI
*O. Allan PRINGLE, *Robert M. NICKLOW and *Ralph M. MOON

*Faculty of Engineering Science, Osaka University
Toyonaka, Osaka 560, Japan

*Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

#Hirosima Institute of Technology
Saeki, Hiroshima 731-51, Japan

*Physics Department, University of Missouri-Rolla
Rolla, Missouri 65401, U.S.A.

*Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831, U.S.A.

ABSTRACT

The Néel temperature $T_N$ of fcc Fe has been measured as a function of pressure to 8.7 kbar by neutron diffraction using a high pressure cell of supported-cylinder type. Cold-pressed zirconia was employed for the material of the cylinder. A sample with 2.77 at% of fcc Fe, precipitated in a Cu matrix, and having precipitates size between 500 and 500 Å, undergoes antiferromagnetic ordering at $67 \pm 2$ K at ambient pressure. With increasing pressure, $T_N$ decreases following a relation: $T_N(K) = 67 - 1.28p - 1.11 \times 10^{-1}p^2 - 6.17 \times 10^{-3}p^3$, where $p$ is in kbar.

INTRODUCTION

The face-centered-cubic phase of iron (fcc Fe) is stable only at temperatures between 910 and 1403 °C at ambient pressure. It can be metastably retained to room temperature by precipitation, alloying, or film deposition. It was neutron diffraction technique that first clarified the magnetic structure of fcc Fe to be antiferromagnetic with the spin vectors inclined at about 19° from the cube axes\(^1\). This structure has long been accepted until a recent finding, also by neutron diffraction, of a complex structure accompanied by a periodic lattice distortion\(^2\).

Recent extensive studies done by another techniques, x-ray diffraction and Mössbauer effect for instance, have elucidated some important characteristics about the antiferromagnetic ordering of fcc Fe:
the ordering temperature $T_m$ is strongly governed by the particle size of the fcc Fe precipitates$^3$; the antiferromagnetic ordering is basically associated with a structural transition$^4$; the structural transition becomes suppressed for precipitates below a critical size (150 Å$^5$) and instead a spin density wave (SDW) state$^6$ appears.

Studies of the effect of pressure on magnetic materials are of great interest because the magnetic properties can drastically change with application of pressure and consequently the effect of volume reduction can simply be derived. Although such volumetric effect can also be induced by alloying, the effect may be complicated by other factors such as electronic, magnetic, and structural contributions. One pertinent study on fcc Fe which yielded the pressure coefficient of $T_m$ to be $-0.5$ K/kbar was from Mössbauer effect measurement of precipitates$^7$. In this case the precipitate size was about 60 Å, being significantly smaller than the critical size for the absence of the structural transition. Thus, there has been no previous study dealing with pressure effect on structural-transition-associated antiferromagnetic ordering of fcc Fe.

This paper reports high pressure neutron diffraction study of fcc Fe particles precipitated in a Cu single crystal. The size of the particles was sufficiently beyond the critical value, ensuring the presence of the structural transition.

**EXPERIMENTAL**

A single crystal of Cu containing 2.77 at% Fe was treated in argon for 5 h at 1000 °C, quenched into water and then aged for 90 h at 650 °C. With the heat treatment, the Fe was present as particles of 500-600 Å (Refs. 2 and 5) in diameter, having the same orientation as the matrix Cu crystal. The crystal was machined into a rod measuring about 9 mm high and 6 mm in diameter so that the crystallographic [001] axis was parallel to the rod axis.

The sample was pressurized in a high pressure cell of supported-cylinder type shown in Fig. 1, following the procedure described elsewhere$^8$. In brief, the sample was encapsuled in a micro cell, together with a KCl crystal for a pressure marker. Flourinert, FC-75, was used as the pressure-transmitting fluid. The capsule was placed in a barrel-shaped cylinder. The use of cold-pressed zirconia for the material of the cylinder made it possible to observe the magnetic peak of

![Fig.1. An exploded view of the high pressure cell.](image)
fcc Fe. It was otherwise disturbed with a powder peak of alumina in the
cell of the standard design\(^9\). After clamping the pressure generated at
room temperature, the cell was cooled to about 10 K. The pressure was
estimated from compression of KCl and the equation of state for this
material.

Neutron diffraction measurements were undertaken on HB3 at HFIR of
Oak Ridge National Laboratory with an incident wavelength of 2.443 Å. A
graphite filter was used to reduce the \(\lambda/2\) intensity. The [001] axis of
the crystal was oriented perpendicular to the neutron scattering plane.

**RESULTS AND DISCUSSION**

An example of intensity contours of magnetic scattering is shown in
Fig.2. The data were taken at 2 kbar and 10.0 K on the (001) scattering
plane. In addition to the magnetic peak of fcc Fe, the contours actually
involve a peak from the matrix Cu as well as background from the cylinder.
A peak at around 1 1 0 is the (220) \(\lambda/2\) reflection of Cu. The magnetic
peak of fcc Fe appears at 1.01 1.01 0. Such contour data were taken at
various temperatures while warming the sample to 80 K which is well above
the Néel temperature of fcc Fe. The magnetic scattering of fcc Fe was
extracted by subtraction of 80 K-data from contours at each temperature.

The peak intensity at various pressures is plotted in Fig.3 as a
function of temperature. At 1 bar prior to the pressurization, \(T_N\) is
located at 67 K, in agreement with previous studies\(^9\),\(^{11}\),\(^{12}\).\(^{13}\),\(^{14}\).
A conspicuous decrease in the intensity is observed with increasing

**Fig.2.** Contour map for magnetic
reflection of fcc Fe.
Numbers on the contours
are in unit of neutron
counts per min.

**Fig.3.** Neutron intensity vs.
temperature for fcc Fe.
pressure. This decrease of the intensity with pressure is in qualitative accord with first-principles calculations\textsuperscript{11,12} that show a rapid decrease in the magnetic moment of fcc Fe with decreasing volume. In Fig. 3, $T_N$ obviously decreases as the pressure is elevated. Upon release of pressure, both the intensity and $T_N$ return nearly to those prior to the compression. The reversible behavior suggests that the particle size of the sample remained essentially unchanged during the pressurization and depressurization.

Figure 4 gives plots of $T_N$ against pressure. The smoothed curve in Fig. 4 follows a relation

$$T_N = 67 - 1.28p - 1.11 \times 10^{-1} p^2 - 6.17 \times 10^{-3} p^3 \quad (1)$$

where $p$ is in kbar. Also shown in Fig. 4 by a dashed line is the result of Mössbauer effect study\textsuperscript{7}.

The pressure coefficient of $T_N$ normalized by the ambient $T_N$ for both the present neutron diffraction and the Mössbauer effect studies are listed in Table I along with those for some other materials. From Fig. 4 and Table I, it is apparent that there are two significant differences between the neutron diffraction and the Mössbauer effect studies: $T_N$ at ambient pressure is higher by about 20 K and the pressure dependence is steeper in this study.

The difference in $T_N$ can simply be interpreted by the difference in the sizes of fcc Fe particles studied. From the size dependence of $T_N$ (Ref.3), such particles of about 60 Å as studied by the Mössbauer effect\textsuperscript{7} can never exhibit $T_N$ higher than 50 K, while particles larger than 500 Å in size (this study) show $T_N$ exceeding 60 K.

In addition, the antiferromagnetic ordering in our sample is accompanied by a structural phase transition\textsuperscript{4,5} whereas in the sample studied by Mössbauer effect\textsuperscript{7} the transition is presumably suppressed because of the particle size smaller than the critical value\textsuperscript{8}.

![Graph showing $T_N$ vs. pressure](image)

**Fig. 4. Antiferromagnetic ordering temperature for fcc Fe.**

<table>
<thead>
<tr>
<th>Material</th>
<th>$(dT_N/dP)/T_N \times 10^{-2}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc Fe</td>
<td>-1.9</td>
<td>This study</td>
</tr>
<tr>
<td>fcc Fe</td>
<td>-1.0</td>
<td>7</td>
</tr>
<tr>
<td>Cr</td>
<td>-1.6</td>
<td>13</td>
</tr>
<tr>
<td>CoO</td>
<td>0.22</td>
<td>14</td>
</tr>
<tr>
<td>FeO</td>
<td>0.34</td>
<td>14</td>
</tr>
<tr>
<td>MnO</td>
<td>0.25</td>
<td>15</td>
</tr>
</tbody>
</table>
Thus, this study is concerned with structural-transition-associated $T_N$ while it is likely that the W"{o}ssbauer effect study\textsuperscript{71} has dealt with $T_m$ accompanied only by SDW state\textsuperscript{99}. The difference in the mechanism producing the antiferromagnetic ordering can be one of the causes which give rise to the difference in the pressure coefficient of $T_N$.

In any event, the normalized pressure coefficient for fcc Fe is quite close to that of Cr\textsuperscript{133} (Table I). In the oxides\textsuperscript{147, 151} shown in Table I, the normalized pressure coefficients of $T_N$ are smaller than those of Fe and Cr by approximately an order of magnitude and are opposite in sign.

In Fig.4, the two lines meet at about 9 kbar, suggesting a possibility that our sample would face the SDW state at pressures higher than 10 kbar.

ACKNOWLEDGMENT

This work was supported by the Department of Energy, U.S.A. and the Ministry of Education, Science, and Culture, Japan under US-Japan Cooperative Program in Neutron Scattering.

REFERENCES

MAGNETIC ORDER IN THE COMPETING INTERACTION STATE OF TERNARY INTERMETALLICS DyMn$_2$Si$_2$ AND DyMn$_2$Ge$_2$

Masayoshi OHASHI, Hideya ONODERA, Takahito ONO', Tetsuo ANDOW', Satoru FUNAHASHI*, Yasuo Yamaguchi and Hisao KOBAYASHI**

Institute for Materials Research, Tohoku University Sendai 980, Japan

*Department of Physics, JAERI, Tokai-mura, Naka-gun, Ibaraki-ken 319-11, Japan

**Electrotechnical Laboratory, 1-1-4 Umesono, Tsukuba, Ibaraki-ken 305, Japan

ABSTRACT

Precise powder neutron diffraction measurements were performed on the rare-earth intermetallic compounds DyMn$_2$Si$_2$ and DyMn$_2$Ge$_2$ with the body-centered tetragonal structure of the ThCr$_2$Si$_2$-type. Both materials have three magnetically ordered phases. The high temperature phase takes the antiferromagnetic order just by the Mn moments along the c-axis, where the Dy moments are disordered. The low temperature phase has the ferrimagnetic structure in which the ferromagnetic layers of the Dy and Mn moments are coupled antiferromagnetically, except canting of Mn moments in DyMn$_2$Si$_2$. The intermediate temperature phase appears between 33 K and 37.5 K for DyMn$_2$Ge$_2$ and between 22.4 K and 36.7 K for DyMn$_2$Si$_2$. The moments modulation magnetic structure along the c-axis is proposed from the magnetic reflections which are observed at not only the nuclear reflection angles but also the satellite positions of the nuclear scattering. (1,0,±δ), (1,0,3,δ), and (1,1,±δ) where -0.66, 0.68. This state is attributed to the competing exchange interactions between Dy-Mn(AF) and Mn-Mn(AF) along the c-axis under strong anisotropy.

INTRODUCTION

Most of the ternary rare-earth intermetallic compounds present address, Research Laboratory, Oki Electric Industry Co.Ltd., Higashiasakawa 550-5, Hachioji, Tokyo 193, Japan
**Present address, Central Research Laboratory, Hitachi Ltd., 1-280 Higashi-koigatuchio, Kokubunji, Tokyo 185, Japan
$RT_2X_2$ (R=rare earth, T=3d, 4d, or 5d transition metal, X=Si, Ge) crystallize in the body-centered tetragonal structure of the ThCr$_2$Si$_2$-type (space group I4/mmm) in which the R, T, and X atoms occupy the 2(a), 4(d), and 4(e) sites, respectively. This structure can be characterized as a sequence of planes composed of the same kind of atoms stacked along the tetragonal axis, R-T-X-R-X-T-X-R (Fig. 1).

![Fig. 1. Crystal structure of DyMn$_2$Ge$_2$ and DyMn$_2$Si$_2$ (ThCr$_2$Si$_2$-type structure) projected along the b axis. The open circles represent atoms at $y=0$ where the solid circles stand for atoms at $y=1/2$.](image)

Only Mn atoms among the 3d transition metals carry magnetic moment in these intermetallics, and order magnetically at relatively high temperature (300-500 K). The magnetic ordering of the R sublattice generally occurs at low temperatures.

In the case of DyMn$_2$Ge$_2$ and DyMn$_2$Si$_2$ (ThCr$_2$Si$_2$-type structure), two magnetic transitions on the ordering of Dy moments have been observed at $T_{c_1}=22.4$ K and $T_{c_2}=37.5$ K for the former, at $T_{c_1}=22.4$ K and $T_{c_2}=36.7$ K for the latter. In the higher temperature range from $T_{c_2}$ to $T_w$, both materials are a collinear antiferromagnet where the Mn moments along the c-axis make ferromagnetic arrangement in the c-plane with antiferromagnetic coupling between adjacent Mn layers. In the low temperature range below $T_{c_2}$, DyMn$_2$Ge$_2$ is a collinear ferrimagnet with antiferromagnetic coupling between ferromagnetic Tb and Mn layers. At the intermediate temperature phase, complex behaviors have been observed. Dy Mössbauer studies have revealed that there exist two kinds of Dy atom with different magnetic state for DyMn$_2$Ge$_2$ and three kinds of Dy atom for DyMn$_2$Si$_2$. Recently, the neutron diffraction study on powder DyMn$_2$Ge$_2$ by Venturini et al. has shown the unexpected occurrence of the coexistence of three magnetic structure in 33-37.5 K temperature range. However, magnetization measurements and Dy Mössbauer study have shown the transition to the intermediate state at $T_{c_2}$ seem to be of first order. Therefore, one can expect the compound to have a single magnetic phase and magnetic structure of interest.

In the present work, in order to settle the magnetic structure in the intermediate temperature state of DyMn$_2$Si$_2$ and DyMn$_2$Ge$_2$, neutron diffraction measurements have been performed on the powdered sample.
EXPERIMENTAL

The purities of Dy and Mn metals in sample preparation were 99.9%, and Ge and Si metals were 99.999% in purity. The compounds were synthesized by a conventional argon arc technique. For ensuring homogeneity, each ingot was turned over and remelted several times, followed by annealing at 1200°C for several days in a magnesia crucible which was sealed in a quartz tube with an appropriate quantity of argon gas. X-ray diffraction measurements on products exhibit only the lines which are characteristic for the ThCr$_2$Si$_2$-type structure. DyMn$_2$(Si$_{8/3}$Ge$_{5/3}$)$_2$ sample was served the purpose of DyMn$_2$Ge$_2$, because the DyMn$_2$(Si$_{8/3}$Ge$_{5/3}$)$_2$ compounds shows similar magnetic transitions to DyMn$_2$Ge$_2$ and has more stretched intermediate temperature range from T$_{C_1}$=26 K to T$_{C_2}$=36 K.

Neutron diffraction experiments were carried out by using the TAS-2 and KSD installed at the thermal neutron guide of the JRR-3M reactor in JAERI. The diffraction patterns were recorded at the temperature 8.0, 25.5, and 100 K for DyMn$_2$Si$_2$ and 30 K for DyMn$_2$(Si$_{8/3}$Ge$_{5/3}$)$_2$ in a wavelength $\lambda$=1.445Å. A special parallel-side thin container was used in order to minimize neutron absorption. The powder samples were sealed in the container with helium gas. The magnetic form factor of Mn and Tb$^{3+}$ ions were taken from Ref. 8.

RESULTS AND DISCUSSION

Neutron diffraction patterns taken at three characteristic temperatures corresponding to each one of three magnetic phases, as shown in Fig. 2.

DyMn$_2$Si$_2$: Above T$_{C_1}$=36.7 K, diffraction lines with (h+k+l)=even are content with R=3% and the position parameter of Si atom z=0.381 in the ThCr$_2$Si$_2$-type crystal structure. Lines with (h+k+l)=odd come from the antiferromagnetic order of the Mn moments of 2.0$\mu$$_{\text{B}}$/Mn where the Dy moments are disordered. This magnetic ordering is common to RMn$_2$X$_2$ and may be described as stacking of ferromagnetic planes of the Mn moments aligned along the c-axis with the sequence ++--+, as shown in Fig.3(a). Below T$_{C_1}$=22.4 K, the diffraction pattern at 8 K shows an increase of the intensity of the nuclear lines and peaks with (h+k+l)=odd. This result was satisfactorily analyzed by the canting-ferrimagnet model, which consisted of ferromagnetic c-planes of Dy with the moments of 10.4$\mu$$_{\text{B}}$/Dy along the c-axis and Mn with the moments of 2.0$\mu$$_{\text{B}}$/Mn coupled antiferromagnetically to the Dy moments. The Mn moments were titled about 60° from the c-axis and the components of Mn moments in the c-planes coupled antiferromagnetically along the c-axis, as shown Fig. 3(b). In the intermediate temperature between T$_{C_1}$=22.4 K and T$_{C_2}$=36.7 K, one observed the disappearance of the peaks with (h+k+l)=odd and additional superlattice line with $K=(0,0,0.66)$, (101)$^-$, (101)$^+$, (103)$^-$ and (110)$^\pm$, besides ferromagnetic superimpose on the nuclear lines. From no satellite reflection of the (002) it follows that each direction of moments is along the c-axis. The longitudinal moment modulation model, as shown in Fig. 3(c), explained
satisfactorily the observed data with R=5%. Each moment of the Dy and the Mn atom is given as follows,

\[ \mu_D = 7.5(\pm 0.2) + 2.9(\pm 0.4) \cos(2\pi K \cdot R + \phi) (\mu_s), \]

\[ \mu_M = -2.0(\pm 0.3) \cos(2\pi K \cdot R + \phi) (\mu_s), \]

where \( \phi = \pi \) is the phase factor between the Dy and the Mn moments. This model can realize three kinds of Dy atom with no full magnetic moment of Dy\(^{3+}\) ion, and makes no contradictory with the Mössbauer study that has revealed three sites of Dy atom, A, B, and C in Ref.6. In the diffraction pattern at 25.5 K, disappearance of the (111) signifies the intermediate temperature state to be a new magnetic phase of moment modulation.

DyMn\(_2\)(Si\(_x\), Ge\(_{2-x}\))\(_2\): Each pattern of the diffraction data taken above \( T_c = 36 \) K and below \( T_c = 26 \) K gives the same magnetic structure as one of the corresponding phase in DyMn\(_2\)Si\(_2\). In the intermediate phase, one finds about the same diffraction pattern obtained in DyMn\(_2\)Si\(_2\) at 25.5 K and also could analyzed by the longitudinal moment modulation model, as shown in Fig.4(a).
The propagation vector is $K = (0, 0, 0.68)$ and each magnetic moment of the Dy and Mn atom is expressed by

![Diagram](a)

![Diagram](b)

![Diagram](c)

Fig. 3 Illustration of the proposed magnetic structure for (a) the high temperature, (b) the low temperature and (c) the intermediate magnetic phase in DyMn$_2$Si$_2$.

![Diagram](a)

![Diagram](b)

Fig. 4 (a) Proposed magnetic structure in the intermediate temperature state of DyMn$_3$(Si$_{0.6}$Ge$_{0.4}$)$_2$, and (b) simplified model proposed by Venturini et al.
\[ \mu_y = 6.4 (\pm 0.5) + 3.7 (\pm 0.7) \cos (2\pi K \cdot R + \phi) (\mu_\text{B}). \]
\[ \mu_x = -2.0 (\pm 0.2) - 2.0 (\pm 0.4) \cos (2\pi K \cdot R + \phi) (\mu_\text{B}). \]

This calculation with \( R=8\% \) could make up two kinds of the Dy moments and complies with the request of the Mössbauer spectroscopy study of Ref.5. Venturini et al. have proposed the intermediate magnetic structure with \( K=(0,0,0.666) \) that made null moment sites of the Dy atom for small moment sites in the present model, as shown is Fig.4(b). It is necessary to measure more precisely both the scattering angle and the intensity of magnetic reflections for comparison between two models.

While they have reported that the intermediate state is the coexistence of three different magnetic phases: the low temperature phase, the intermediate phase and the high temperature phase. The present diffraction pattern have no (111) reflection referred to the antiferromagnetic ordering of the Mn moments that is found in the high temperature phase. Then this intermediate temperature state seems to be not the magnetic coexistence one but the single magnetic phase. One could attribute these moment modulation state to the competing exchange interactions between Dy-Mn (AF) and Mn-Mn (AF) along the c-axis under strong anisotropy.

ACKNOWLEDGEMENTS

The authors would like to thank Messrs. N.Minakawa, Y.Shimojo and K.Nemoto for assistance in neutron diffraction experiments.

REFERENCE


— 409 —
MAGNETIC PHASE TRANSITION OF CsNiCl₃

Katsunori UBUKATA, *Toshiya INAMI, *Kazuhisa KAKURAI
and Mitsuhito MOTOKAWA

Department of Physics, Faculty of Science
Kobe University, 650 Kobe, Japan

*Institute for Solid State Physics
University of Tokyo, 106 Tokyo, Japan

ABSTRACT

In this contribution we would like to report the preliminary results on sublattice magnetization of CsNiCl₃, a quasi one-dimensional (1-D), S=1, antiferromagnetic (AF) Heisenberg system with weak easy axis anisotropy, near its spin flop field. A comparison with a more classical system CsMnI₃ with S=5/2 indicates, that the fine structures observed in the sublattice magnetization of this S=1 system may be related to the quantum nature of the system.

Phase transitions in triangular lattice antiferromagnets have been studied extensively both theoretically and experimentally.1,2) Recently Kawamura showed that the phase transitions in layered triangular lattice antiferromagnets belong to new universality classes associated with the chiral degeneracy.3) Experimental evidences for this new universality classes have been also found4) and are in good agreement with the predictions of the Monte Carlo simulations.5) Moreover Kawamura et al.6) predicted that the critical behaviour of ABX₃ in finite fields is also described by this new type of chiral universality. They performed detailed analysis of the critical behaviour in finite fields by using a scaling theory. For the systems with easy-axis anisotropy, two successive phase transitions observed in a field H, T_Ni(H)(i=1,2), are merging into a single phase transition T_Ni(H) at a multicritical point. In the vicinity of the multicritical point, these three phase boundaries are characterized by an anisotropy-crossover exponent \( \phi \) associated with n=3 chiral class as

\[ |H-H_m| \propto (T_{Ni}(H) - T_m)^\phi, \quad i=1,2,3 \]

where the multicritical point is denoted by \((T_m, H_m)\). Kawamura predicted that \( \phi \) is close to unity: \( \phi \approx 1.06 \). Recently experimental evidences for this theoretical prediction have been reported in several ABX₃ systems with easy-axis anisotropy, namely for CsNiCl₃,7) CsNiBr₃,8) and CsMnI₃.9)

On the other hand, detailed dynamical studies in ABX₃ with different spin values S have demonstrated, that the quantum effect really affects the spin dynamics in the 3-D ordered state.10) As reported elsewhere the spin dynamics of the ordered state in S=1, CsNiCl₃ and S=5/2 CsMnI₃ are very different.11) It is therefore very surprising at first sight that such a general law for the multicritical point based on the classical treatment should be valid.
To shed some light on the nature of this phase transitions in the extreme quantum case and classical case we started to study sublattice magnetizations in CsNiCl₃ and CsMnI₃ near their spin flop field by means of neutron scattering.

The systems: CsNiCl₃ and CsMnI₃

ABX₃ systems we are concerned here have a hexagonal lattice structure, spacegroup D₆h, with lattice constants given in Table 1. There are two formula units per unit cell. The magnetic moments of the B²⁺ ions are strongly coupled along the c-direction by the intrachain interaction J. The larger distance between the chains in the basal plane results in a weak interchain coupling J'. The spin Hamiltonian is given by

\[ H = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j - J' \sum_{ij} \vec{S}_i \cdot \vec{S}_j - D \sum_i (\vec{S}_i^z)^2 + g_\mu_B H \sum_i \vec{S}_i^z \]

where the first and second sums are over nearest-neighbour along the chain and in the basal plane, respectively. D is the single site anisotropy and the last term is the Zeeman energy in an applied field H along the c-axis. In Table 1 the characteristic parameters for CsNiCl₃ and CsMnI₃ are listed.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Lattice constants[Å]</th>
<th>S</th>
<th>Anisotropy</th>
<th>Tₐ[K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsNiCl₃</td>
<td>a=7.18   c=5.93</td>
<td>1</td>
<td>easy axis</td>
<td>Tₐ₁=4.84, Tₐ₂=4.40</td>
</tr>
<tr>
<td>CsMnI₃</td>
<td>a=8.20   c=6.96</td>
<td>5/2</td>
<td>easy axis</td>
<td>Tₐ₁=11.42, Tₐ₂=8.20</td>
</tr>
</tbody>
</table>

Table 1: ABX₃ systems investigated in this study.

Both systems have an easy axis anisotropy (D>0) and there are two phase transitions in zero applied field. The intermediate phase for Tₐ₁>Tₐ₂ where only the component of the moments along c-direction order. The magnetic structure below Tₐ₂ has been determined by neutron diffraction in the case of CsNiCl₃. The ordered spins lie in a plane containing one of the hexagonal symmetry direction and the c-direction. The spins are ordered antiferromagnetically along the chain direction. On one third of the chains the spins are aligned along the c-axis and on the other chains they are canted at an angle of ±θ away from the c-axis. In the classical theory this canting angle is determined by the ratio of J' and D. For the isotropic case the angle θ is 60°. In the ordered state the system has three domains due to the sixfold symmetry in the basal plane.

Experimental Results and Discussions

The experiments were carried out on the triple axis spectrometer PONTA installed in the reactor hall of JRR-3M at JAERI, Tokai. Since the magnetic field has to be applied along the easy axis direction, i.e. in c-direction and since the AF peaks appear at points like Q=(n/3,n/3,l) with n=1,2,.. and l=1,3,..., one has to apply the field in the scattering plane to study the spin flop phase transition. Therefore the use of an horizontal field cryomagnet is mandatory. The single crystal sample was oriented with its [110] and [001] axis in the scattering plane and mounted in the superconducting horizontal field cryomagnet. Because of the limited access
angles for the horizontal field cryomagnet, only the \((1/3, 1/3, 3)\) magnetic Bragg peak using a neutron wavelength of \(1\)\(\AA\) was studied.

Figure 1a) and b) show the sublattice magnetization measured at \(Q=(1/3, 1/3, 3)\) in CsNiCl\(_3\) with a) increasing and b) decreasing magnetic field. The step around \(2\)\(T\) associated to the spin flop transition is clearly observed. In details small steps below the main flop filed \(H_{sf}\) can be seen at \(0.5T\) and \(1.4T\) (indicated by the arrows).

![Graph](image)

Figure 1: Sublattice magnetization in CsNiCl\(_3\) as measured at \(Q=(1/3, 1/3, 3)\) with a) increasing and b) decreasing field. The lines are guides for the eye.

The step at lower field is clearly seen in both increasing and decreasing field, whereas the step at \(1.4T\) is not significant in the measurement with decreasing field. Instead a tail of the intensity after the spin flop down to this field value is observed.
In fig. 2 the sublattice magnetization of CsMnI₃ is depicted at $Q=(1/3,1/3,3)$ with increasing field. The spin flop field is nearly at 6T and can be just reached with the horizontal field cryomagnet. In contrast to CsNiCl₃ case, a gradual increase in the sublattice magnetization is seen up to the spin flop field.

Classically spin flop fields are expected to be at

$$h_{sf} = \sqrt{4AK} \quad \text{with} \quad A=4JS, B=6J'S, K=D_S \quad \text{and} \quad h=g\mu_B H.$$  

Inserting the exchange parameters $J$ derived from the inelastic neutron scattering experiments one obtains the following anisotropy parameters, as shown in the last column of Table 2.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CsNiCl₃</td>
<td>-16.6</td>
<td>-0.1</td>
<td>≤0.035</td>
<td>1.95</td>
<td>0.031</td>
</tr>
<tr>
<td>CsMnI₃</td>
<td>-9.5</td>
<td>-0.045</td>
<td>0.042</td>
<td>5.3</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Parameters as determined by inelastic neutron scattering$^{13,14}$

Table 2: The microscopic parameters for CsNiCl₃ and CsMnI₃. The last column shows the anisotropy parameters derived from the observed spin flop fields.

Table 2 also shows the anisotropy parameter $D$ as obtained from the dispersion relation perpendicular to the chain direction.$^{13,14}$ These values are consistent with those derived from the spin flop fields.

Figure 3 shows the expected intensity variation of the $(1/3,1/3,3)$ magnetic peak according a classical vector model with the parameters of CsMnI₃. The experimentally observed smooth increase of the intensity below the spin flop field is well reproduced and the intensity ratio of the
intensity after the spin flop transition and the initial intensity of 2.46 is in good agreement with the experimentally observed 2.4.

Recently Shiba et al. suggested a pre-spin flop transition in the classical 120° AF structure, where a 90° rotation of the AF structure within the ca-plane is predicted. The theoretical prediction of this pre-spin flop field is

\[ h_{c1} = 4AK \left( 1 - \sqrt{\frac{B}{2A}} \right), \]

with A, K and h as defined above and B = 6J'/S.

Inserting the above microscopic parameters (Table 2), the pre-spin flop fields are expected to be at 1.83T and 4.98T for CsNiCl₃ and CsMnI₃ respectively. They are supposed to be very close to the main spin flop transitions in both cases. Furthermore, a rough estimation of the intensity change at (1/3,1/3,1/3) according to this type of pre-spin flop transition in ca-plane shows, that the change is very small indeed and may be not observable in this experiment.

Therefore the two steps in CsNiCl₃ can be most probably not explained by this mechanism. A rough estimation of the possible transverse field component due to the misalignment of the c-axis to the field direction (experimentally determined to be less than 2°) excludes the single domain formation responsible for the additional step. Considering the fact that these low field sublattice magnetization steps are not seen in CsMnI₃, a nearly classical spin system with S=5/2, it is suggestive that these fine structures in the sublattice magnetization in CsNiCl₃ may be associated with the quantum nature of the S=1 system. Because of the finite spin value, the number of the possible spin states are finite. Hence these steps can be the expression of the discrete nature of the quantum spin state. Further detailed studies to clarify this aspect are in preparation and a theoretical approach to study such an extreme quantum case is asked for.

In summary, we have observed fine structures in the sublattice magnetization of S=1 AF system CsNiCl₃ near its spin flop transition. A comparison with S=5/2 AF system CsMnI₃ indicates, that these fine structures may be associated with the extreme quantum nature of this S=1 AF system.
Acknowledgement: We would like to thank Professor Shiba informing us the results of his calculations prior to publication. This research was supported in part by the Grant in Aid for the Scientific Research Project of the Japanese Ministry of Education, Science and Culture.

References:

MAGNETIC PHASE TRANSITION OF CsCuCl₃ IN PULSED MAGNETIC FIELD

Michinobu MINO, Katsunori UBUKATA, Takahiro BOKUI, Masatoshi ARAI,
*Hidekazu TANAKA and Mitsuhiro MOTOKAWA

Department of Physics, Faculty of Science, Kobe University,
Nada, Kobe, 657 Japan

*Department of Physics, College of General Education, Nagoya University, Furo-cho, Chikusaku, Nagoya, 464-1 Japan

ABSTRACT

Neutron diffraction measurements of a triangular lattice antiferromagnet CsCuCl₃ have been done in a pulsed high magnetic field up to 14T. The field applied parallel to the c-axis and it is observed that the reflection intensity at (1/3 1/3 0.085), which corresponds to the low field magnetic structure, abruptly decreases at Be=10T, where the magnetization shows a small jump. Above Be, a new reflection at (1/3 1/3 0) appears. These results are consistent with a model that a new type of magnetic phase transition occurs due to the quantum effect.

INTRODUCTION

CsCuCl₃ is one of the hexagonal ABX₃ type compounds. The magnetic properties have been studied by many researchers.¹-⁵ It has linear chains of Cu²⁺ ions along the c-axis and they make triangular lattices in the c-plan. The intrachain coupling is ferromagnetic, whereas the interchain coupling is antiferromagnetic. Below Tₘ=423K, a structural phase transition due to the cooperative Jahn-Teller effect occurs, and it causes the antisymmetric Dzyaloshinsky-Moriya interaction between spins along the c-axis. This compound shows a 120° magnetic structure in the c-plane and have a long pitch helical spin structure along the c-axis below Tₘ=10.5K.¹ It has been experimentally found that the magnetization has a small jump at Be=12.5T at 1.1K in a field parallel to the c-axis.³ It has been difficult to explain this phase transition for a long time within the classical theory. Recently, a new theoretical interpretation for this small jump has been proposed by Shiba and
Fig. 1 Spin structures (a) the umbrella-like structure below $B_c$; (b) the coplanar structure proposed above $B_c$ by Shiba's model.

Nikuni. They have pointed out that the quantum fluctuation is very important in CsCuCl$_3$, because CsCuCl$_3$ has $s=1/2$ spins. They propose a model that the umbrella-like structure changes to the coplanar structure at $B_c$ as shown in Fig. 1 as an applied field is increased. In this mode, two spins are parallel while one is opposite. This kind of magnetic phase transition have never been observed. We have studied neutron diffraction experiments in a pulsed high magnetic field in order to investigate the magnetic structure of this material.

EXPERIMENTS AND DISCUSSIONS

The experiments were made using a spallation neutron source at KENS. To generate pulsed magnetic fields, a water cooling Bitter magnet were employed. Field production was repeated every two second and a duration time of about 1 m second. In our experiments, the time of flight (TOF) diffraction method was used. In order to observe the Bragg reflection in a high field, pulsed fields were synchronized with the beam pulses of neutron. The sample was mounted in a flow type cryostat which was set at the center of the magnet. The magnetic field was applied along the c-axis. The measurement were done at 7K. At this temperature, phase transition field $B_c$ is 10T.

The intensities of the magnetic reflection (1/3 1/3 0) and (1/3 1/3 0.085) were measured as a function of the magnetic field, because a magnetic unit cell is three times as large as a chemical one in the c-plane. First we focus our attention on the (1/3 1/3 0.085) reflection. This reflection is due to the component of the magnetic moments perpendicular to the c-axis. In addition to the 120° structure at zero field, the umbrella type structure like Fig. 1(a) in the c-plane at low field, this spin system has a helical modulation along the c-axis which makes a satellite along the c*-axis in the reciprocal lattice space. The field dependence of the intensity decreases as an field is increased, below $B_c$ as shown in Fig. 2. This is due to the decrease of the perpendicular component of the moments in an increasing field and the calculated intensity is in good agreement with the experimental result. It shows an abrupt

---

417
Fig. 2 (1/3 1/3 0.085) reflection intensity as a function of a magnetic field. The dotted line is the calculation from the model.

decrease at $B_c$ and a gradual change above it. Assuming the model shown in Fig. 1(b), we calculated the field dependence of the intensity above $B_c$ which is shown by the dotted line in Fig. 2, and we found very good coincidence between the experiment and calculation. The intensity becomes very small when an applied field is close to the saturation field $B_s=27$T reflecting decrease of the perpendicular component.

On the other hand, the (1/3 1/3 0) reflection is due to the parallel components of the magnetic moments to the c-axis. At the umbrella type structure below $B_c$, the c-components of all the magnetic moments are identical and the reflection must appear at (1 1 0). This reflection

Fig. 3 The diffraction patterns of (1/3 1/3 0) (a) $B=8.5$T below $B_c$; (b) $B=13.2$T above $B_c$. 

— 418 —
Fig. 4 (1/3 1/3 0) reflection intensity as a function of a magnetic field. The dotted line is the calculation from the model.

overlays on the nuclear reflection and it is difficult to be discriminated from the strong nuclear one. Therefore (1/3 1/3 0) reflection can not be observed below Bc. Above Bc, however, the proposed structure shown in Fig.1(b) contributes to (1/3 1/3 0) reflection. Figure 3(b) shows the (1/3 1/3 0) reflection observed at 13.2 T. This magnetic reflection disappears below Bc as shown in Fig.3(a). We calculated the field dependence of the intensity for the proposed structure and found a very good agreement between calculation and the experimental result as shown in Fig.4.

CONCLUSION

In order to study the magnetic structure of CsCuCl3, neutron diffraction experiments have been made in a high magnetic field. At a phase transition field Bc, a suddenly decrease of the intensity of magnetic (1/3 1/3 0.085) reflection and the appearance of (1/3 1/3 0) are observed. The determined magnetic structure is consistent with the structure which is suggested by a new model with the quantum fluctuations.

ACKNOWLEDGMENTS

We would like to thank Professor H. Shiba and Dr. H. Nojiri for valuable discussion.
REFERENCES

7) T.Nikuni and H.Shiba: to be published.
DYNAMIC MAGNETIC RESPONSE OF A GAP-TYPE KONDO MATERIAL CeNiSn

M. Kohgi, K. Ohoyama, T. Osakabe, M. Kasaya, T. Takabatake# and H. Fujii#

Department of Physics, Tohoku University, Sendai 980, Japan
#Faculty of Integrated Arts and Science, Hiroshima University, Hiroshima 730, Japan

ABSTRACT

The magnetic response of the gap-type Kondo system CeNiSn was studied by means of neutron inelastic scattering. No well defined crystal field excitations were observed. Instead, the spectrum is composed of a Lorentzian-like response centered at $E=0$ and a broad peak around 4-7 meV which develops strongly below about 15 K. The results indicate that the 4f electron state in this system is more like valence-fluctuating and that the anomalous temperature dependence of the peak corresponds to the development of a short range magnetic correlation at the low temperatures.

INTRODUCTION

The $\epsilon$-TiNiSi type inter-metallic compound CeNiSn attracts attention because of its anomalous magnetic and transport properties. The compound shows no magnetic ordering down to 0.4 K. Its electrical resistivity shows a Kondo-like anomaly above about 100 K though strongly anisotropic. The magnetic susceptibility, which is also anisotropic, shows clear deviation from that expected for a trivalent Ce compound. However, its temperature dependence is rather strong. These experimental results indicate that this system is located just on the boundary of the VF regime and the Kondo regime. More interestingly, the compound shows additional anomalies below about 10 K which are characterized by the gap formation at the Fermi energy. The energy gap was estimated to be about 6 K. No clear
explanation for the origin of the gap formation has been given yet. We performed neutron scattering experiments on CeNiSn to investigate the 4f electron states in this material from the microscopic point of view.

EXPERIMENTAL DETAILS

A polycrystalline sample of CeNiSn of about 60 g was used in the experiment. The inelastic neutron scattering experiments were performed on the chopper spectrometer INC and the crystal analyzer spectrometers LAM-D and LAM-40 at KENS. In the experiments at the INC spectrometer, the incident neutron energy was chosen at 60 meV. The resolution (FWHM) was 3.3 meV at elastic position (E=0). The LAM-D and LAM-40 spectrometers employ several large-solid-angle energy-focusing type analyzers composed of pyrolytic graphite, each with its own beryllium filter and detector and with final energy of 4.6 meV. LAM-D views an ambient temperature water moderator, whereas LAM-40 views a solid-methane moderator. Thus, the former has a high sensitivity at the energy transfer of the thermal energy region, whereas the latter at the lower energy region, but with same resolution of 0.35 meV (FWHM) at E=0.

RESULTS AND DISCUSSION

Figure 1 shows the result of the inelastic magnetic response of CeNiSn at about 20 K at the INC spectrometer. The data were taken in the low angle bank of detectors (2θ = 5° to 12°). The raw data were corrected for monitor normalization, background subtraction, absorption correction and detector efficiency, and put to the absolute scale by using the data obtained for a vanadium standard sample. The phonon contribution in the raw data was estimated from the high scattering angle (∼120°) data and subtracted from the low angle data3).

Fig. 1 Magnetic response of CeNiSn at about 20 K observed with the INC spectrometer. The solid curve indicates the results of the least squares fitting to the data using a Lorentzian as the spectral function. Insets show the raw data and the estimated phonon contribution.
The insets in the figure shows the raw data and the estimated phonon contribution. The obtained magnetic response is rather structure-less above about 5 meV. The solid curve in the figure shows the best fit to the data using a single Lorentzian centered at E=0 as the spectral function. The fit gives the width of 2.2 meV.

Figure 2 shows the spectra of CeNiSn at 3 and 15 K measured with the LAM-D spectrometer at the scattering angle of 35°. The raw data were corrected for the wavelength variation of the incident spectrum, detector efficiency and absorption effect. No correction was done for phonon contribution because of the limited Q range which is covered by the LAM-D spectrometer. The result shows that the spectrum below about 10 meV is not a monotonous function of energy but has a peak at about 4 meV which is strongly temperature dependent and cannot be seen in the INC data at 19 K because of the resolution limitation of the spectrometer. The overall features of the spectrum above about 10 meV is not so different from the raw data of the INC experiment (see the inset in Figure 1). The apparent difference between the two cases is due to the difference of the scattering triangles, of phonon contribution and of the resolution.

Figure 3 shows the response functions of CeNiSn at 3, 15 and 50 K at small energy transfer measured with the LAM-40 spectrometer. After the same correction as the case of LAM-D data, the raw data, each of which is the sum of the counts at 24°, 40°, 56° and 72° detectors, were corrected for the $k_f/k_i$ term and the temperature factor $\hbar \omega / [1- \exp(-\hbar \omega \beta)]$ in the cross section to get the response function ($=$ Im[χ(Q,ω)/ω] + phonon background). In this correction, we neglected the resolution effect because it is small enough for the present purpose. The data at the energy transfers less than 0.7 meV are omitted in the figure because of the strong contamination of the incoherent elastic scattering. The broken line in the figure indicates the phonon contribution estimated from the measurement on LaNiSn with the same experimental condition as the measurement on CeNiSn. The phonon contribution is clearly small in this energy region. The overall height of the observed magnetic response function decreases with increasing temperature. This is
qualitatively consistent with the behavior of the reported temperature dependence of the bulk susceptibility. Each spectrum below about 2.5 meV increases monotonically with decreasing energy transfer though a small hump is seen around 1.1 meV. The solid, dotted and chained lines in the figure show the best fit Lorentzian function centered at $E=0$ to the data between 0.7 and 2.5 meV at 3, 15 and 50 K, respectively. The agreement is rather good in the energy region. The obtained widths of the Lorentzians are 1.6, 2.1 and 3.0 meV, respectively. Note that the width of 2.1 meV at 15 K is comparable to the result of the Lorentzian fit to the INC data at 19 K which gives the width of 2.2 meV. However, the spectra show more complicated features at higher energy transfer. At 3 K, the spectrum starts to deviate from the Lorentzian above about 2.5 meV and show a broad peak around 4 meV. At 15 K, the spectrum also shows broad peaks around 4.5 to 7 meV, as also seen in the LAM-D data (Figure 2). However, the intensity around 4 meV is considerably smaller than that at 3 K, whereas the intensity around 7 meV is the same as that at 3 K. At 50 K, no peak is seen around 4 meV. Instead, the spectrum starts to deviate from the Lorentzian around that energy.

The present results show that no well-defined crystal field excitations are seen for CeNiSn. Instead, it shows a Lorentzian-like broad response centered at $E=0$ with a broad peak at about 4 meV. The magnetic response might be ascribed to that of over-dumped crystal field excitations, but, it is difficult to explain the strong temperature dependence of the peak around 4 meV by a simple model. Anomalous spectra for CeNiSn were also reported by other groups, but the agreement with our results is not satisfactory. It is clear, anyhow, that the hybridization effect in CeNiSn is strong and that its 4f electron state is more like valence fluctuating, because no well defined crystal field excitations were observed. We suggest that the anomalous temperature dependence of the peak around 4 - 7 meV indicates the
development of a short range magnetic correlation at the low temperatures, and that it corresponds to the gap formation phenomena in this system.

References


MAGNETIC PHASE DIAGRAM OF OXYGEN NONSTOICHIOMETRIC LA$_2$NiO$_{4+\delta}$

T.OMATA, K.YAMADA, K.NAKAJIMA, *S.HOSOYA and Y. ENDOH

Department of physics, Tohoku University, Sendai, Japan

ABSTRACT

Present neutron scattering and magnetization measurements reveal that LA$_2$NiO$_{4+\delta}$ provides lots of varieties of physical properties, in particular in magnetism, as a function of the excess oxygen concentration. Observed experimental results resolved the complexity in the magnetic phase diagram of the previous works. At least three different antiferromagnetic phases separated by the biphase regions are discovered in the present concentration range. In particular the samples with $\delta$ larger than about 0.1 exhibit a new type of magnetic ordering with the in plane cycloid-type incommensurate modulation.

1.INTRODUCTION

LA$_2$NiO$_4$ is one of typical materials of the two dimensional (2D) square lattice antiferromagnet with spin value S=1. Such compounds are conventionally called 2-1-4 system and LA$_2$CuO$_4$, a progenitor of the high Tc superconducting copper oxide, belongs to the same family. The crystal structure of these compounds is called T-type structure, where octahedron formed by six oxygen atoms with a 3d metal cation at the center determines the symmetry of the crystal. It is well known that the crystal structure and magnetic structure of these compounds are closely related in each other and that oxygen non-stoichiometry strongly affects the physical properties of the system. Many experimental studies on LA$_2$NiO$_4$ were carried out, but the results are rather complicated and contain many discrepancies. These complexities mainly come from the difficulty in controlling the oxygen stoichiometry of the specimens. The systematic study using samples with correctly regulated oxygen content is indispensable to make these problems clear. LA$_2$NiO$_{4+\delta}$ has wider excessive oxygen solubility range compared with other 2-1-4 systems and the $\delta$ value can be widely varied by annealing in the reductive or oxidizing atmosphere. In other words, this material is a good example to investigate the effects of the excess oxygen on various physical properties systematically and quantitatively. We attempt to make clear the process of oxidizing in this system and finally to compile the detailed magnetic phase diagram versus $\delta$ of this system. We obtained a number of important and new facts of the physical properties of the whole system and made the origin of complexity in the previous studies clear.

*Permanent address: Institute for Materials Research, Tohoku University, Katahira, Sendai, Japan
2. EXPERIMENT

In all the experiments performed in this study, the single crystals grown by means of floating zone method were used. Single crystal La$_2$NiO$_4$ always contains excess oxygen from stoichiometry in the as-grown state. We adopted CO+CO$_2$ mixed gas for the reduction because of its high thermal stability and N$_2$+O$_2$ mixture for oxidation. The anneal was carried out for 4 hours at 1000°C. We could obtain single crystals of δ range between 0 and 0.15 in the present study. The average δ value of the specimens were determined by the conventional iodimetry titration.

The magnetization measurements were carried out using both the vibrating sample magnetometer (V.S.M.) and the SQUID magnetometer (MPMS, Quantum Design) for the samples annealed as above. The measurement was performed within the temperature range of 4.2-300K with the applied external magnetic field 0-2T. The SQUID magnetometer could be used in the temperature range 5 to 350K and the external field 0 up to 1T.

Neutron diffraction experiments were performed for the single crystals of the size 0.1-1cc on the Tohoku University Neutron Scattering Spectrometer of TUNS and TOPAN installed at JRR-2 and JRR-3M of Tokai Establishment, JAERI respectively. The incident neutrons were monochromated by Ge (311) reflection at TUNS and by pyrolytic Graphite (002) TOPAN. The temperature of the sample was controlled between 10K and room temperature with the resolution of ~1% using He- closed cycle refrigerator (cryogenics CTI, Lake Shore).

3. RESULT

3.1 Stoichiometric La$_2$NiO$_4$

Since details of stoichiometric La$_2$NiO$_4$ were described in our separate paper$^1$), we only summarize characteristic features here. We experimentally confirmed that the Neel temperature of stoichiometric sample is 328K (Fig.2(a)) and that the structural transition occurs at $T_s$=70K, from the orthorhombic Bmab phase to the tetragonal P4$_2$/nmc or the orthorhombic Pccn with small orthorhombicity. The previously proposed spin structure with Bmab crystal structure$^2$) is shown in Fig.1. Here the spin direction [100] is perpendicular to the direction of the tilt of the NiO$_6$ octahedron, therefore canting Ni spins out of the NiO$_6$ plane should not occur. Due to the structural transformation, the magnetization shows a sudden jump (Fig.3) caused by a net weak ferromagnetic moment along [001]. A spin reorientation which allows the spin canting occurs at $T_s$ (Fig.2(c)) and consequently the weak ferromagnetism appears in the low temperature phase.

![Fig.1) Crystal structure of La$_2$NiO$_4$ (a). The small arrows denote the displacement of oxygen atoms.
Schematic drawing of the NiO$_6$ octahedron tilt in Bmab phase (b) and P4$_2$/nmc or Pccn (c). The arrows denote the spin direction of Ni ion.](image-url)
3.2 The effect of excess oxygen

As shown in M-T curves for samples with $0 \leq \delta \leq 0.014$ (Fig.3), a tiny change in $\delta$ value causes a drastic change in magnetic properties of this system. The small amount of excess oxygen smears the jump of the moment at $T_S$, showing that the low temperature structural transition is very sensitive to the excessive oxygen. As decreasing the weak ferromagnetic component, another anomaly becomes noticeable around 210K. The field cooled magnetization measurement for $\delta=0.014$ detects an appreciable weak ferromagnetic moment between 70 and 210K. However a small kink still exists at 320K.

![Magnetic reflection intensity plots](image)

**Fig.2)** The temperature dependence of magnetic reflection intensity at (0,1,1) (a-f), (0.73,0,0) (g) or (0.725,0,0) (h).

![Magnetization plots](image)

**Fig.3)** Magnetization under 1Tesla field parallel to [001] for the 1Tesla field cooled samples with various $\delta$.

The temperature dependence of magnetic (011) intensity for the sample with $\delta=0.014$ from the neutron diffraction (Fig.2(b)) exhibits a discontinuous decrease on warming. There seems to exist two distinctive phases which have different $T_N=320$ and 210K corresponding to two anomalies observed by the magnetization measurement. The anomaly at 210K can be concluded the Neel temperature of the new phase. Therefore, the excessive oxygen does not change the $T_N$ drastically in the original phase, but induces another phase with different $T_N$ and different oxygen content. The phase separation occurs even in a very dilute oxygen concentration region such as $\delta=0.008$. Here we define a stoichiometric one as phaseI and the excess oxygen induced phase with $T_N=210$K phaseII. The peak profile of nuclear (400)/(040) for $\delta=0.001$ showing tripled peak above $T_S$ cannot be explained by twin structure of single orthorhombic crystal, such a reflection pattern suggests the coexistence of multi-phases of phaseI and phaseII. For
δ=0.018, we obtained a specimen composed of almost single phase of the phaseII. The (011) magnetic intensity almost disappears at TNII=210K, and a small fraction of intensity come from phaseI remains up to 320K (Fig.2(c)). Corresponding to the TNII=210K, a broad peak in magnetization appears (Fig.3) and a weak ferromagnetic moment exists below this temperature. The existence of the weak ferromagnetism shows that phaseII has a spin canted magnetic structure as in the case of low temperature phase of stoichiometric one, though the crystal structure of phaseII seems to be orthorhombic with a smaller distortion from the line width of the nuclear reflections. Although there is no change in fundamental La2NiO4 -type spin structure, the phaseII has a different magnetic structure with a different spin canting due to a broad peak in magnetization at TN and the weak ferromagnetism observed below this temperature.

Judging from the (011) intensity in the neutron diffraction experiments (Fig.2(d)), we concluded that the phaseI which has TN of over 300K does not exist for δ>0.02. The (011) intensity indicates that there occurs a discontinuous change again, while the magnetization exhibits two peaks corresponding to two step decrease in the magnetic intensity. The specimens in the region 0.02<δ<0.07 also consist of two phases as in the region 0<δ<0.02. In this region, the specimens are composed of two phases with the Neel temperature 90K and 180K. The one with TN=180K is identical to the phaseII and 90K is a new oxygen richer phase induced by further oxidation. Different from phaseII case, the appreciable increase of weak ferromagnetic moment was not detected at 90K. The phaseIII is thought to have a spin structure without spin canting, or with canting which alters its sign in the adjacent layer.

As we described above, three distinctive phases with different magnetic ordering successively appear in different oxygen content. The excess oxygen content of respective phases are δ=0, 0.02 and 0.07. Observed nuclear peak width indicates that the phaseII and phaseIII have crystal structure with less orthorhombicity than phaseI at T>Tc. We will make further structural refinement to distinguish the phaseII and phaseIII.

3.3 A new phase with incommensurate spin modulation

Up to δ=0.1 the fundamental La2NiO4-type spin structure was conserved. On the other hand, the magnetic properties drastically change in the region δ>0.1. The specimen of δ=0.126 has the magnetic reflections splitted on the reciprocal space. This splitting indicates that the magnetic order of this system is modulated with an incommensurate periodicity. The temperature dependence of the intensity for the one of splitted reflection (0.725,0,0) is shown in Fig.2(g). It has a critical transition at TN=110K. Corresponding to the Neel temperature, the magnetization in the 2D plane exhibits a sharp divergence (Fig.4). The fact implies that the stable single phase material exists in the vicinity of this δ value. A new phase appears by the doping excess oxygen in such a high oxygen concentration region. The splitting of the magnetic peak in q is 0.275(r.l.u.) which corresponds to the modulation period of about 3.64 lattices and the direction of the modulation is parallel to the splitting vector Δd=(0.275,0,0) for δ=0.126. A probable model for this modulation is either the spin density wave or the helical structure in 2D plane (cycloid). Since we observed intense magnetic reflections on the scattering vector Q=(h,0,0) which is prohibited in the stoichiometric La2NiO4-type structure, where spin direction S is parallel to scattering vector Q, this structure must contain the modulation for the spin direction. Therefore, the cycloid type structure rotating in the a-b plane is most likely. Such a magnetic reflection can be explained for using the spin structure presented in Fig.5.
One NiO$_2$ plane at $z=0$ is depicted in this figure, where arrows are the moment of the Ni ion, the square at the center, the magnetic unit cell in this plane and dashed arrow represents the propagation vector of the cycloid-type modulation. The original spin structure is the La$_2$NiO$_4$-type, and the interplane nearest coupling is ferromagnetic. One unique cycloid type modulation is taken along [100] in one domain. We conclude here a new type of the spin modulation as described above within the oxygen concentration range $0.12<\delta<0.152$. It should be noted that the Neel temperature changes as $\delta$ increases. Although the splitting of the magnetic reflection is varied with $\delta$, the intensity pattern seems to be unchanged and thus the modulation in the 2D plane remains essentially unchanged.

4. SUMMARY

We present the magnetic phase diagram for La$_2$NiO$_4+\delta$ system compiled from our experimental result (Fig.6). We mark here that the $\delta$ value described is the average value in a whole specimen. We confirm at least the existence of three phases with different oxygen content at $\delta=0$, $\delta=0.02$ and $\delta=0.07-0.10$ separated by two mixture-phase regions. The oxygen concentration and physical properties of the single phase of phase I and phase II are expected to vary very little. In these two phase regions, the oxygen concentrations of both phases are almost unchanged but the volume fraction is shifted. The total oxygen content $\delta_{\text{tot}}$ was determined from the existing ratio of each phase, that is

$$\delta_{\text{tot}} = \delta_{P_i} + \delta_{jP_j},$$

where $\delta_{i,j}$ and $P_{i,j}$ denote excess oxygen concentration and existing ratio of the phase $i,j$, respectively. Though the existence of other phases with much smaller fraction cannot be discarded completely, the continuous change upon introduce of excess oxygen which have been expected was not observed in this system. Thus we concluded a discontinuous change caused from a phase separation in this study. Most of the results in previous reports can be explained by the appearance of three phases. The stoichiometric La$_2$NiO$_4$ (phase I) has the spin structure without spin canting as was previously proposed between the temperature range $T_S<T<T_N$ and it transforms into the spin-canted structure below $T_S$. 

— 430 —
La$_2$NiO$_4$+$\delta$

![Graph showing the magnetic phase diagram of La$_2$NiO$_4$+$\delta$, with T$_N$ as a function of $\delta$.](image)

The former report about the weak ferromagnetism above the structural transition temperature, or the large peak at Neel point in the magnetic susceptibility as a function of temperature, must be related to the phaseII induced by very small discrepancy of oxygen stoichiometry. The accurate control of oxygen stoichiometry is therefore very important in the study on these compounds. In La$_2$CuO$_4$-system, the spin canting structure at antiferromagnetic phase is also confirmed experimentally. On the other hand, such a spin canting has not been observed in La$_2$CoO$_4$-system. The appearance of spin canting is a balance of the D-M interaction and the single ion anisotropy in the system. The weak anisotropy easily allows spin canting in order to gain the D-M energy in cuprate. A severe competition of two energies causes the various transformation from non-spin-canted phase to spin-canted phase in La$_2$NiO$_4$-system.

In any way, the fundamental La$_2$NiO$_4$-type spin structure $S/a$, $\tau/a$ is sustained until $\delta=0.1$. The $\delta$ value is a very large compared with the La$_2$CuO$_4$-$\delta$ system case, where oxygen dope of $\delta=0.02$ suppresses the three dimensional long range order (LRO) and makes this system metallic and superconducting. Generally, the doped hole as a result of introducing excess oxygen destroys antiferromagnetic exchange interaction between magnetic ions and therefore diminishes the Neel temperature. This frustration in nickelate system seems to be less effective than in cuprate system. The highly localized character of the doped holes in nickel compounds is one possible factor to sustain the magnetic LRO.

The specimens in the two mixture-phase regions in this phase diagram are composed of only two phases suggesting the existence of miscibility gap in this region. Such a miscibility gap already suggested for this system. 3),4)

A interpretation of existence of phases with discrete $\delta$ value is argued by connecting with the excess oxygen ordering$^5$),6). However, we could not detect such an extra oxygen superstructure. The ordering of oxygen, therefore, may be realized in an narrow local region of the sample. Moreover, the long range oxygen order in small excess oxygen region such as $\delta=0.02$ corresponding to our phaseII, cannot be detected and therefore it might not be realized. If oxygens order in such a dilute region, the mixture region composed of a quasi-continuous change will occur in the vicinity of $\delta=0$. That is incompatible with our result. Another suggestion for the phase separation is given by Baird et al.$^7$ considering the electronic structure in Nd$_{2-x}$Ce$_x$CuO$_4$ system. They execute a tight binding calculation as a function of the electron doping level and discussed that the competing requires of the Madelung energy and the electronic energy cause two different crystal geometries which give infinitesimal orbital energies and consequently a phase separation takes place into two phases of the different geometry. They pointed out that the crystal geometry and electronic structure is closely related.
In our results, the most exciting difference from the previous studies is that we confirmed a single phase material and the existence of the incommensurate order phase in $\delta > 0.12$, where this system was thought to have no magnetic order previously. In the range of $\delta > 0.12$ we confirmed the three dimensional magnetic LRO with the cycloid type modulation. The Neel temperature increases as increasing oxygen concentration $\delta$ in this area. It is a rather peculiar tendency that the doped oxygen sustain the magnetic LRO. Such a modulated spin structure is realized by spin Hamiltonian taking long ranged next nearest neighbor exchange with the nearest neighbor interaction. Here let us suppose the spin as a classical vector (Fig 7). The spin Hamiltonian is,

$$\sum_{nn} J_{nn} s_i \cdot s_j + \sum_{nnn} J_{nnn} s_i \cdot s_j$$

here $J_{nn}$ denotes exchange between nearest neighbor spin and $J_{nnn}$, next nearest neighbor. If $J_{nn} < 2J_{nnn}\cos \delta$, then the modulated spin structure should be stabilized. The norm of the propagation vector of the incommensurate modulation is

$$|k| = \frac{a}{2\pi} \cos^{-1} \left( \frac{J_{nn}}{2J_{nnn}} \cos \delta \right)$$

where $a$ is the lattice constant. From our experimental result, $\cos \theta = 44.5^\circ$ and $\cos \delta = 5^\circ$, $J_{nn}/J_{nnn}$ is estimated to be 1.44 for the sample with $\delta = 0.126$. The doped hole works to enhance next nearest neighbor exchange.

To conclude, we made the oxidizing process of La$_2$NiO$_4+\delta$ system clear throughout our experimental studies. We observed many important new facts about the physical properties of this system owing to the systematic investigation using minutely regulated specimens. However, a lot of interesting subjects is not elucidated yet, such as the crystal symmetry of the phase II and phase III, dynamical property of oxygen doped system or the nature of peculiar transition of incommensurate phase and so on. Further information will be obtained in the future neutron experiments.
REFERENCES

7) N. Colin Baird and Jeremy K Buedett  Physica C 168 (1990) 737-646
SPIN WAVE EXCITATIONS IN A KONDO MATERIAL CeCu$_2$

Masahumi Kohgi, Toyotaka Osakabe, Yukio Morii†, Satoru Funahashi†,
Yoshichika Onuki‡ and Hideki Yoshizawa*

Department of Physics, Tohoku University, Sendai 980, Japan
†Department of Physics, Japan Atomic Energy Research Institute,
Tokai, Ibaraki 319-11, Japan
‡Institute of Material Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan
*Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106,
Japan

ABSTRACT

The low lying magnetic excitations in the Kondo lattice CeCu$_2$ were studied at the temperatures below the Néel temperature by means of neutron inelastic scattering. Rather well-defined spin wave excitations were observed below about 1.5 meV along the principal axes in the a*-b* reciprocal lattice plane. The excitation energy is nearly constant along the [ξ,0,0] direction with the energy around 1.4 meV, while it shows a dip down to the energy of about 0.7 meV along the line [ξ,1/2,0]. From the scattering vector dependence of the cross-section of the excitation, it is concluded that the spin fluctuations in the antiferromagnetic phase of CeCu$_2$ are mainly along the a-axis direction.

INTRODUCTION

The intermetallic compound CeCu$_2$, which has the orthorhombic crystal structure of the space group type of Imma, is characterized as a Kondo lattice compound. It shows typical Kondo anomalies such as -logT resistivity or a large electronic specific heat$^{1-3}$. De Haas van Alphen experiment shows the presence of conduction electrons with large cyclotron effective masses$^4$. It undergoes an
antiferromagnetic ordering below $T_N = 3.5$ K. The ordered magnetic moment and magnetic entropy at $T_N$ of a Ce atom are, however, reduced from the expected values for a Ce$^{3+}$ ion in the crystal field$^{5,6}$. These facts indicate that there exists a sizable effect of the competition between the single-site Kondo effect and the inter-site RKKY exchange interaction in this system. In order to study the competition phenomena from the microscopic point of view, we have performed the measurement of the low lying magnetic excitations at the temperatures below the Néel temperature by means of inelastic neutron scattering. In this paper, some preliminary results are reported.

EXPERIMENTAL

The sample is a single crystal of CeCu$_2$ with the diameter of about 5 mm and the length of about 5 cm. It was grown by the Czochralski method in a helium gas atmosphere of 1.5 kg/cm$^2$. The neutron scattering experiment was performed on the triple axis spectrometer TAS1 at JRR3M reactor, JAERI. The measurement was carried out with the fixed incident neutron energy of 13.7 meV. A pyrolytic graphite filter was inserted in the incident beam path in order to eliminate the effect of the higher order contamination. The beam collimation before the monochromator is about 1 degree. The horizontal collimation after the monochromator was chosen as 40'-40'-40'.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the peak intensity of the 110 Bragg reflection. The result indicates the development of the antiferromagnetic long range ordering below 3.5 K with the same periodicity as that of the chemical lattice. This is in good agreement with the previous report$^6$.

The inelastic scattering measurements were carried out in the $a^* - b^*$ reciprocal lattice plane.
Fig. 2 Spectra of Constant Q scans at (a) $(\zeta, 1, 0)$ and (b) $(\zeta, \zeta, 0)$ at 1.5 K.

Rather well defined neutron groups were observed below about 1.5 meV. Since the crystal field excited levels (at 9 and 23 meV\textsuperscript{7}) are far above this value, these excitations are ascribed to the spin wave scattering. Figures 2(a) and (b) show the observed constant-Q spectra at 1.5 K with $Q=(\zeta, 1, 0)$ and $(\zeta, \zeta, 0)$, respectively. The solid circles in the figure 2(a) show the data at 4.2 K. The solid lines are the results of the least squares fit to the data using a sum of two Gaussians as the resolution broadened scattering functions of the spin wave scattering as well as the incoherent elastic scattering. The dispersion relations of the spin wave excitations at 1.5 K obtained from the least squares fit are shown in Figure 3. The excitation energy is nearly constant along the $[1,0,0]$ direction around 1.4 meV, while the data along the other directions show that there is a dip of the excitation energy down to about 0.7 meV along the line $[\zeta, 1/2, 0]$. The scattering intensity of the excitation is roughly proportional to the square of the sine of the angle between the scattering vector and the $[1,0,0]$ direction.
Fig. 3 Obtained dispersion relations of spin wave excitations at 1.5 K.

From the obtained spin wave dispersion relations, it is concluded that the exchange interaction is dominant along the b-axis. This may reflect the chain structure of the nearest neighbor Ce atoms along b-axis. However, the observed dispersion relation along the b-axis is anomalous since the spin wave excitation energy is maximum at the zone center. The observed scattering vector dependence of the spin wave cross section indicates that the spin fluctuation is mainly along the a-axis. This strong anisotropy of the spin fluctuations in the antiferromagnetic state is in good accordance with the anisotropy of the magnetization below $T_N$ and the bulk susceptibility at high temperatures where the a-axis is also the easy direction.\(^5\) These phenomena may reflect the anisotropy of the crystal field in this system. As for the Kondo problem, it is suggested that the single site Kondo effect in this system is rather weak compared to the RKKY exchange interaction, since the spin wave excitations in this system are found to be well-defined. Thus, the reason of the Kondo anomalies seen in the low temperature properties of this system is still not clear. More detailed neutron scattering work is under way.
References

POWDER NEUTRON DIFFRACTION STUDY ON
\( \text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta}(\delta=0.0 \text{ AND } 1.67) \)

* Hideshi FUJISHITA, *Masatoshi SAITO, 
*Yukio MORII and #Satoru FUNAHASHI

* Department of Physics, College of Liberal Arts 
Kanazawa University, Kanazawa-city, 920 Japan

*Department of Physics, Faculty of Science 
Nagoya University, Nagoya-city, 464-01 Japan

# Department of Physics, JAERI 
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

Powder neutron diffraction patterns of \( \text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+\delta} \) (\( \delta = 0.0 \) and 1.67) were analyzed by Rietveld method. For \( \delta = 0 \), it had been indicated, by powder X-ray diffraction, that the structure was a monoclinic one. The R factors of the present analysis for the monoclinic structure were about 3/4 of those for the previous orthorhombic ones. The structure was almost the same as the previous X-ray result except \( z(02) \). For the annealed phase, the tetragonal and the orthorhombic structures had been presented by X-ray diffraction and by neutron diffraction, respectively. The R factors of the present analysis for the orthorhombic structure were about 5/6 of those for the tetragonal structure. The distance between the Pb plane and the oxygen deficient Cu plane was found to become larger in proportion to \( \delta \), though there occurs a phase separation in low \( \delta \) region.

INTRODUCTION

Much attention has been paid, from several points of view, to high-\( T_c \) superconductors with the formula \( \text{Pb}_2\text{Sr}_2\text{ACu}_3\text{O}_{8+\delta} \) (\( A \) is a mixture of \( \text{Y} \) or lanthanide and alkaline-earth metal) with \( T_c \) about 70K.1,2 One of the points is an interesting structural similarity to the \( \text{Ba}_2\text{ACu}_3\text{O}_{6+\delta} \) superconductors. Noticing this point, Ohta and Maekawa examined the electronic configurations in the compounds with \( A = \text{Y}_{1-x}\text{Ca}_x \) through the calculation of the
Madelung energy in the ionic model.\textsuperscript{3) } They presented the carrier distributions and the phase diagrams.

In this paper we report results of crystal structure analyses of \( \text{Pb}_2\text{Sr}_2\text{YCuxO}_8+\delta \) (\( \delta = 0 \) and 1.67) by powder neutron diffraction, where \( \delta = 0 \) was used according to Cava et al.\textsuperscript{1) } for the samples quenched from 860° C to room temperature. The \( \delta = 1.67 \) was estimated from weight increase for the samples annealed at 400° C in air. It has already turned out that the \( \delta \) does not change continuously\textsuperscript{4,5) } and the system remained as insulator.\textsuperscript{4) }

The orthorhombic structures with space group \( \text{Cmmm} \) were first proposed for \( \text{A} = \text{Nd}_{0.76}\text{Sr}_{0.24} \) and \( \text{Y} \) with \( \delta = 0 \) by single crystal X-ray diffraction\textsuperscript{1) } and powder neutron diffraction,\textsuperscript{6) } respectively. However electron diffraction experiment carried out later by the same group indicated a slight distortion from the \( \text{C} \) centered structure.\textsuperscript{7) } The orthorhombic structure with space group \( \text{P2_12} \) was also proposed for \( \text{Pb}_2\text{Ba}_2\text{YCu}_3\text{O}_8 \) by electron diffraction and powder neutron diffraction.\textsuperscript{8) } The orthorhombic structure with \( \text{Pman} \) was recently presented for \( \text{Pb}_2\text{Sr}_2\text{Y}_{0.73}\text{Ca}_{0.27}\text{Cu}_3\text{O}_8 \) by single-crystal neutron diffraction.\textsuperscript{9) }

We have carried out structure analysis of \( \text{Pb}_2\text{Sr}_2\text{YCuxO}_8 \) by powder X-ray diffraction, and found evidence of monoclinic lattice distortion with \( \beta = 90.23° \).\textsuperscript{4) } We have analyzed the structure using monoclinic space groups \( \text{P2_1/m} \) and \( \text{P2_1} \). Almost the same fits to the observed pattern were obtained for both space groups. The fractional coordinates obtained for \( \text{P2_1/m} \) were almost same as those obtained from powder neutron diffraction\textsuperscript{6) } except \( z(02) \).

Though the formal expressions of the structures cited here seem different each other at first sight, the structures are almost identical because almost all of atoms sit on the symmetrically special positions. The distortion from the structure with \( \text{P4/mmm} \) is caused by the silt of only one symmetrically independent oxygen atom in \( \text{PbO} \) layers. Then we used the space group \( \text{P4/mmm} \) for the sample with \( \delta = 1.67 \) in the analysis of powder X-ray diffraction, because it was found to have tetragonal lattice.\textsuperscript{4) } However orthorhombic structure with space group \( \text{Pmmm} \) was presented for \( \delta = 1.47 \) by powder neutron diffraction.\textsuperscript{5) }

We made powder neutron diffraction on \( \text{Pb}_2\text{Sr}_2\text{YCuxO}_8+\delta \) (\( \delta = 0 \) and 1.67) to obtain more precise structural information than those obtained by powder X-ray diffraction and to know the change of the structure in the annealed phase: The results for \( \delta = 0 \) were almost same as the previous X-ray results\textsuperscript{4) } except \( z(02) \). The fit using \( \text{Pmmm} \) was better than the fit using \( \text{P4/mmm} \) to the observed pattern for \( \delta = 1.67 \). It was found, by the combination with the previous result for \( \delta = 1.47 \), that the lattice parameter \( c \) and the distance between the \( \text{Pb} \) plane and the oxygen deficient Cu plane changed proportionally in the single phase region of the annealed phase.
EXPERIMENT

The compound Pb$_2$Sr$_2$YC$_3$O$_8$ was synthesized by the method basically presented by Cava et al.\textsuperscript{1)} The sintered pellets were quenched on the Cu plate from 860° C. We assume the value of $\delta = 0$ for this quenched samples based on the report by Cava et al.\textsuperscript{1)} Many pellets of these samples were, then, annealed at 400° C for 24h in air. The value of $\delta = 1.67$ was determined for them from the weight increase after the annealing.

Neutron diffraction patterns were obtained using a high resolution powder diffractometer (HRPD) with 64 detectors installed at JRR-3M in JAERI. Incident neutron wave length was 1.823A. The collimation was 6'-20'-6'. A vanadium sample cell was used to avoid diffraction peaks from the cell. Powder specimen was rotated at room temperature during the measurement to prevent a preferred orientation effect. The intensity data were collected at about 0.05° step(2θ) and the data in the 2θ range of 25.8-155° were used for analysis.

The diffraction patterns were analyzed by the Rietveld method using a computer program RIETAN applied to multicountered system. The background level was also fitted by a polynomial expression through the analysis. We have calculated the $R$ factors in two different ways: In defining $R_p = \Sigma \left| y_i(\text{obs})-y_i(\text{cal})/\Sigma y_i(\text{obs}) \right|$, for example, we use two kinds of $y_i(\text{obs})$, raw counted number, $y_i(S+BG)$ and and $y_i(S+BG)-\text{background}$. These two kinds of $R$ factors are distinguished by the subscripts $S$ and $(S+BG)$, where $R_pS$ is always considerably larger than $R_p(S+BG)$.

RESULTS

The orthorhombic structures with space group Cmmm (No.65)\textsuperscript{6)} and P2$_1$2$_1$2$_1$(No.17)\textsuperscript{8)} had already been proposed for Pb$_2$Sr$_2$YC$_3$O$_8$. We have found evidence of monoclinic lattice distortion and analyzed the structure using monoclinic space groups P2$_1$/m (No.11) and P2$_1$(No.4) by powder X-ray diffraction.\textsuperscript{4)} Recently the orthorhombic structure with Pmmm (No.62) was also presented by single-crystal neutron diffraction independently.\textsuperscript{9)}

The presently obtained powder neutron diffraction pattern was analyzed using the orthorhombic Cmmm and P2$_1$2$_1$2$_1$ first. Almost same fits to the observed pattern were obtained for the both space groups. The $R$ factors were $R_{wp}(S+BG) = 19.2\%$, $R_p(S+BG) = 15.3\%(R_pS=29.9\%)$ and $R_{IS}=10.3\%$.

The result of profile fit using the monoclinic P2$_1$/m or P2$_1$ is shown in Fig.1. Almost same fits to the observed pattern were obtained in both cases. The $R$ factors were $R_{wp}(S+BG) = 14.2\%$, $R_p(S+BG) = 11.0\%(R_pS=21.5\%)$ and $R_{IS}=7.6\%$. The lattice parameters refined were $a=5.3867(2)$, $b=5.4262(2)$, $c=15.7252(6)$A and $\beta = 90.23(1)^\circ$ (or $\beta '\approx 89.77(1)^\circ$). The structural parameters are published elsewhere. Constraint was used for positional parameters to reduce the number of parameters in the analyses. The con-
straint means the lattice assumed here has the orthorhombic symmetry with the monoclinic angle $\beta$. The difference between these two structures is only the arrangements of oxygen atoms in PbO planes: The structure with $P2_1/m$ has disordered arrangement and the structure with $P2_1$ has ordered one.

Fig. 1. Neutron Rietveld refinement pattern for $\text{Pb}_2\text{Sr}_2\text{YC}_{\text{u}3}\text{O}_{8}$. The monoclinic space group $P2_1/m$ or $P2_1$ was used.

There are seven monoclinic space groups with non-C centered symmetry including the above two. (Remaining five space groups are $P2_1/c$ (No.14), $P2/c$ (No.13), $P2/m$ (No.10), $Pm$ (No.6) and $P2$ (No.3).) Absent reflections for electron diffraction reported by different groups\(^7,8\) contradicted each other. The contradiction was fairly reduced by some assumptions and the above two space groups were plausible choices.\(^4\) In the present analysis we examined the neutron diffraction pattern for all of the seven space groups without the constraint for positional parameters. The structure with $P2_1/c$ or $P2/c$ could not explain the pattern. Almost same fits to the observed pattern were obtained in the other cases. The $R$ factors were $R_{wp}(S+BG)=13.5\sim 14.2\%$ and $R_p(S+BG)=10.5\sim 10.9\% (R_pS=20.4\sim 21.2\%)$.

In the previous study, we analyzed the X-ray diffraction pattern of $\text{Pb}_2\text{Sr}_2\text{YCu}_2\text{O}_{8.67}$ using the space group $P4/\text{mmm}$ (No.123).\(^4\) However the orthorhombic structure with space group $Pmmm$ (No.47) was presented for $\delta=1.47$ by powder neutron diffraction.\(^5\) Then we analyzed the present neutron diffraction pattern using the both space groups. The result of profile fit is shown in Fig. 2 for $Pmmm$. The $R$ factors were $R_{wp}(S+BG)=12.8\%$, $R_p(S+BG)=10.0\% (R_pS=27.7\%)$ and $R_f=15.8\%$ for $P4/\text{mmm}$, and $R_{wp}(S+BG)=10.8\%$, $R_p(S+BG)=8.4\% (R_pS=23.5\%)$ and $R_f=10.4\%$ for $Pmmm$. The orthorhombic lattice parameters refined were $a=3.8473(2)$, $b=3.8516(3)$, $c=15.8566(5)$ A. The structural parameters are published elsewhere. The fit using $Pmmm$ was meaningfully better than the fit using $P4/\text{mmm}$.
Fig. 2. Neutron Rietveld refinement pattern for Pb$_2$Sr$_2$YC$_3$O$_9.67$. The orthorhombic space group Pmmm was used.

DISCUSSION AND CONCLUSIONS

The monoclinic structure of Pb$_2$Sr$_2$YC$_3$O$_8$ with $\beta=90.23(1)^\circ$ was confirmed by the present neutron diffraction again in addition to the previous X-ray diffraction. The R factors of the present analysis for the monoclinic structure are about 3/4 of those for the orthorhombic structure. The positional parameters obtained for the monoclinic P2$_1$/m or P2$_1$ are almost same as those obtained by X-ray diffraction except $z$(02).

The structural parameters for the orthorhombic Cmm agrees quite well with those obtained by the previous neutron diffraction, though the space group was not accurate. The estimated standard deviations(e.s.ds.) are different several times each other. The difference was mainly brought about by the different way of calculation for e.s.ds. Accurate estimation of standard deviation was pointed out to be difficult in the Rietveld method. The present e.s.ds. were obtained by the method described in ref.11.

It was plausible that the more accurate monoclinic space group for Pb$_2$Sr$_2$YC$_3$O$_8$ was either P2$_1$/m or P2$_1$: The choice was based on some assumptions for results of electron diffraction studies which contradict each other. The unique determination of the structure remains unsolved also by the present neutron diffraction. The difference between these structures, however, is only the arrangements of oxygen atoms in PbO planes: The structure with P2$_1$/m has disordered arrangement and the structure with P2$_1$ has ordered one.

In the previous study, we analyzed the X-ray diffraction pattern of Pb$_2$Sr$_2$YC$_3$O$_9.67$ using the space group P4/mmm, because it had tetragonal lattice. However the orthorhombic structure with space group Pmmm was presented for $\delta=1.47$ by powder neutron diffraction. The present analysis
of neutron diffraction pattern indicated that Pmmn is more accurate space

group from view points of fit and e.s.d.s. of parameters, though the lat-
tice parameters are almost tetragonal (|a-b|/a=1.1x10^-3).

Comparison of the structures of Pb2Sr2YCu3O8+δ (δ=0 and 1.67) is ill-
ustrated in Fig.3a by projections on the ac plane and (110) plane, respec-
tively. The structure with P21/m is shown for δ=0. Changes of inter-
plane distances are schematically shown in Fig.3b.

Fig.3a. Projections of structures of Pb2Sr2YCu3O8+δ (δ=0 and
1.67) on the ac plane and (110) plane, respectively. The
structure with P21/m is shown for δ=0. Open, hatched and
solid symbols indicate the y to be 0.0, 1/4 and 1/2 respec-
tively for δ=0. The oxygen atoms with z~1/2 for δ=1.67
drawn by different hatched symbols have different depth along
the direction perpendicular to the (110) plane.

Fig.3b. Schematic representation of the changes in interplane
distances in Pb2Sr2YCu3O9.67 compared with Pb2Sr2YCu3O8. The
values are indicated in A unit. The + or - sign indicates the
expansion or contraction of the distance, respectively.
We can see the expansion of interplane distances between the oxygen deficient Cu plane and the Pb plane in Pb$_2$Sr$_2$YCu$_3$O$_{9.67}$. Contraction of interplane distance is also be noticed between the Pb plane and the Sr plane. These changes are almost confined in the PbO-CuO$_x$ block, "charge reservoir" in ref.3. In combination with the previous neutron and X-ray study, the variations of the lattice parameter c and the distance between the Pb plane and the oxygen deficient Cu plane are shown in Fig.4 as the increase of $\delta$. The distance was found to become larger in proportion to $\delta$, though there occurs a phase separation in low $\delta$ region.

![Graph](image)

Fig.4. Changes of the lattice parameter c(open circle) and the distance between the Pb and the Cu(O) plane(solid circle) with the change of $\delta$ in Pb$_2$Sr$_2$YCu$_3$O$_{9.67}$. Date other than the solid circle at $\delta=1.67$ were cited from ref.5. Difference of the error bars are mainly caused by the different way of the calculation for the estimated standard deviations. The solid line through the solid circle shows the least squares fit to the circles. The right side and the left side ordinate have the same scale with different origins. The system shows the phase separation in low $\delta$ region.

ACKNOWLEDGMENTS

This work was partly supported by Grant-in-Aid of Scientific Research on Priority Areas of the Ministry of Education, Science and Culture. This work was also partly supported by Grant-in-Aid of Scientific Research(02452070) of the Ministry of Education, Science and Culture.
REFERENCES


MAGNETIC ORDER IN TERNARY COMPOUNDS
TbMn$_2$Ge$_2$ AND TbMn$_2$Si$_2$

Setyo PURWANTO, Masayoshi OIHASHI, Hideya ONODERA, *Yukio MORII,
*Satoru FUNAHASHI, Hiroshi YAMAUCHI and Yasuo YAMAGUCHI

IMR Tohoku Univ., 2-1-1 Katahira, Sendai, Miyagi 980, Japan
*Department of Physics, JAERI, Tokai-Mura, Ibaraki-ken, 319-11 Japan

Abstract

High resolution powder diffraction studies were made on the rare-earth compounds TbMn$_2$Ge$_2$ and TbMn$_2$Si$_2$ with the body-centered tetragonal structure of the ThCr$_2$Si$_2$ type. For TbMn$_2$Ge$_2$, two magnetically ordered phases were observed. In the temperature range of $T_c=95.3K<T<T_N=414K$, Mn moments are only coupled antiferromagnetically along the c-axis. At $T_c=95.3K$, Tb moments become abruptly ordered in a collinear ferrimagnetic state, Tb and Mn moments are coupled antiparallel to each other along the c-axis, and keep the same magnetic structure down to 8K. These results support the Shigeoka's report but make a denial of the magnetic transition and structure proposed by the Leciejewicz and Szytula. TbMn$_2$Si$_2$ takes canted-ferrimagnetic structure below $T_c=54.3K$ with a tilting angle 42° from the c-axis at 6K for Mn atoms while Tb moments are parallel to the c-axis (9.0μ$_B$/Tb and 1.8μ$_B$/Mn at 6K). In the temperature range from $T_c=54.3K$ to $T_N=64.5K$, TbMn$_2$Si$_2$ exhibits a moment modulation structure of wave vector $k=[0,0,0.666]$. Higher than 64.5K to $T_N=550K$, only Mn moments coupled antiferromagnetically.

INTRODUCTION

Intermetallic compounds represented by the formula RM$_2$X$_2$ (where R is a rare-earth, in here is Tb, M is transition metal of 3d or 4d metal, in here is Mn, and X is Germanium or Silicon) crystallize in the body-centered tetragonal structure with the space group D$_{4h}$-I$_4$/mmm, as shown in Fig.1. The R, M, and X atoms occupy at the 2(a), 4(d), and 4(e) positions, respectively. The structure consists of atomic layers perpendicular to the c-axis stacked with the sequence R-X-M-X-R.

![Fig.1 Structure Crystal of RM$_2$X$_2$ compounds](image-url)
TbMn$_2$Ge$_2$ in the previous studies by means of magnetization measurements and neutron diffraction measurements, has Néel temperature of an antiferromagnetic ordering of Mn moments $T_N=413K$\textsuperscript{1}, 414K\textsuperscript{2}, and Tb moments ordering temperature $T_c$, 33K\textsuperscript{3}, 110K\textsuperscript{1} and 95K\textsuperscript{2}, which are scattered. Shigeoka\textsuperscript{3} reported that TbMn$_2$Ge$_2$ at $T=77K$ takes a collinear-ferrimagnetic structure, in which Mn moments couple ferromagnetically along the c-axis and make antiferromagnetic coupling with Tb moments, as shown in Fig.2(a). In this model, the magnetic ordering of Tb moments is followed by the re-orientation of Mn moments, at which the antiferromagnetic interlayer coupling of Mn sublattices changes to a ferromagnetic one. On the other hand, Leciejewicz and Szytula\textsuperscript{1} reported that the collinear antiferromagnetic ordering observed at higher temperature, whose ferromagnetic layers made up of the Mn moments have antiferromagnetic coupling along the c-axis, persists down to 4.2K. Their ferrimagnetic structure around 77K, as shown in Fig.2(b), differs from Shigeoka's model in the magnetic coupling between Tb and Mn moments. Furthermore, they reported that Tb moments makes unusual inclination from the c-axis below 26K, as shown in Fig.2(c). The details have not been clearly established yet.

Fig.2 Magnetic structure model of TbMn$_2$Ge$_2$( a)Shigeoka\textsuperscript{3}, b) and c)Leciejewicz and Szytula\textsuperscript{1})

In TbMn$_2$Si$_2$, two magnetic transitions in the process of making order on Tb magnetic moments have been observed at 53K and 65K\textsuperscript{4}. Shigeoka et al.\textsuperscript{4} determined the magnetic structure in TbMn$_2$Si$_2$ by measurements of magnetization of single crystal and powder neutron diffraction as shown in Fig.3. The Tb moments order ferromagnetically below 65K while the Mn sublattice remains antiferromagnetic. This coexistence model is similar to the Lecciejewicz and Szytula's one in the magnetic structure of TbMn$_2$Ge$_2$ between 26K and 110K.
Below 53K, this collinear ferrimagnetic structure is transformed into the non-collinear one by canting of Mn moments. In the coexistence model of ferromagnetic Tb sublattice and antiferromagnetic Mn sublattice, Tb magnetic moment stands at the center of the antiferromagnetic Mn netting and is anticipated to become to frustrate.

Figure 3 Magnetic structure model of TbMn$_2$Si$_2$ (Shigeoka$^4$)

The present study report on detailed of high resolution powder diffraction measurements for both TbMn$_2$Ge$_2$ and TbMn$_2$Si$_2$ compounds. In the case of TbMn$_2$Ge$_2$, it is clear the magnetic structure of this compound takes the same structure as Shigeoka’s finding down to T=8 K and make denial to the Leciejewicz and Szytula’s model. TbMn$_2$Si$_2$ compound at low and high temperature takes the same structure like Shigeoka’s finding but not for the intermediate temperature. Present study has found a new model for the intermediate temperature.

EXPERIMENTAL PROCEDURES

The sample of TbMn$_2$Ge$_2$ and TbMn$_2$Si$_2$ were prepared by arc melting, under purified argon atmosphere. Melting was repeated several times to insure the homogeneity of product. Then the sample, for TbMn$_2$Ge$_2$, was annealed at 1150°C for 7 day. For TbMn$_2$Si$_2$ was not annealed because the melted sample has shown a good sample without any impurity lines. X-ray diffraction using Fe-Kα radiation shows the ThCr$_2$Si$_2$-type crystal structure and gives the lattice parameter $a=3.960\AA$, $c=10.732\AA$ for TbMn$_2$Ge$_2$, $a=3.912\AA$, $c=10.457\AA$ for TbMn$_2$Si$_2$. High resolution powder neutron diffraction measurements were performed by using HRPD installed at JRR-3M reactor in JAERI. The wavelength of neutron is 1.823Å reflected from (331) plane of Ge crystal$^9$. Magnetic form factor of Mn and Tb$^{3+}$ ions were taken from E.J Lisher and J.B. Forsyth$^6$. 

---

---
RESULTS AND DISCUSSION

TbMn$_2$Ge$_2$: Neutron diffraction patterns taken at temperatures 8K, 35K and 125K are shown in Fig.4. The present data are quite different with the previous study by Leciejewicz and Szytula but rather similar to the Shigeoka’s work. Above 95K, diffraction lines with (h+k+l)= even are analyzed by the ThCr$_2$Si$_2$-type crystal structure. The (111) reflection come from the antiferromagnetic structure of the Mn moments which is a stacking of ferromagnetic Mn planes with the Mn moments aligned in the direction of the c-axis with the sequence +--++. The reliability factor is R=7.8%. The position parameter of Ge atom become to 0.370. And the Mn ions have the moment of 1.8$\mu_B$/Mn.

Fig.4 HRPD pattern of TbMn$_2$Ge$_2$ at 8K,35K and 125K.
Notice that the present diffraction pattern at 125K includes weaker peaks of impurity than the data at 293K reported by Leciejewicz and Szytula.

Diffraction pattern at 8K and 35K come to the same property, except data at 8K show weak additional peaks around 2θ=13° and 34° which correspond the (100)m and (111)m in the Leciejewicz and Szytula’s pattern at 4.2K. After well annealed at 1150°C for 7 days, these peaks become almost disappeared. Therefore, these reflections below 26K obtained by Leciejewicz and Szytula is considered to be related to magnetic state of impurity. Below 95K, one observes only an increase of the intensities of the nuclear lines. The (111) due to the antiferromagnetic coupling of the Mn moments could not be observed. A collinear ferrimagnetic structure, in which the ferromagnetic Tb and Mn layers are coupled antiferromagnetically and both moments aligned in the direction of the c-axis, is confirmed below 95K. R-value become 6.3% when the magnetic moments of Tb and Mn are 9.0µB/Tb and 1.8µB/Mn, respectively.

TbMn2Si2: Neutron diffraction patterns taken between 6K and 80K (see Fig.5.). The present neutron diffraction results at 6K and 78K indicated in agreement with the previously published on powder neutron diffraction study by Shigeoka. TbMn2Si2 takes a canted ferrimagnetic below T=54.3K. In the neutron diffraction pattern are clearly shown the (001) and (003) line, these superlattices lines give a tilting angle of Mn moments from the c-axis, where Tb moments are ferromagnetically order aligned in the c-axis. The refined results give the tilting angle is 42° at 6K, Tb and Mn moments value are 9.0µB/Tb and 1.8µB/Mn, respectively. The neutron diffraction data above T=64.5K has been shown that TbMn2Si2 exhibits a simple antiferromagnetic structure where Tb moments are disordered. In pattern at T=78K, the superlattices lines can be indexed by (111) and (113) due to the Mn moments in antiferromagnetic order. The refinement confirms the ThCr2Si2-type crystal structure with zSi=0.380 and the reported antiferromagnetic structure with the Mn moment of 1.8µB/Mn.

The present neutron diffraction pattern at 58.3K indicate a different results with the previously published by Shigeoka. One observes four new additional superlattice lines, besides the (111) and the ferromagnetic superimpose to the nuclear lines. It can be described by a sum of three sub patterns implying the coexistence of three different magnetic phase: the first, the low temperature phase in which the magnetic contribution affects only the (hkl) nuclear reflections satisfying the condition h+k+l=even, the second, the high temperature phase, here, the magnetic ordering of the Mn sublattice only contributes to the appearance of the superlattices lines (hkl) with h+k+l=odd, the third, the intermediate phase, related to the new superlattice line. These additional magnetic lines can be indexed on a magnetic unit cell with â=a and ç=3c, (10 1/3), (10 2/3), (10 1/2) and (11 3/4). No magnetic contribution to the (006) peaks indicate that the magnetic moments also aligned along the c-axis in the intermediate state. Simplification of Ono model[7] turns out a new intermediate magnetic structure model as shown in Fig.6. In this model, the ferromagnetic Mn layers are piled up with the sequence +---+---+ along the c-axis, and make antiferromagnetic and ferromagnetic Mn blocks. When strong antiferromagnetic interaction between Dy and Mn moments and Ising like property are assumed, Dy3+ ion takes a full moment in the ferromagnetic block and become to frustrate in the antiferromagnetic block. Refinement due to the coexistence of three magnetic state give the results that the population of low temperature phase : intermediate phase : high temperature
Fig. 5 HRPD pattern of TbMn$_2$Si$_2$ at 6K, 58.3K and 78K

phase is 3 : 4 : 3 and Tb and Mn moment are 9.0 $\mu_B$/Tb and 1.8$\mu_B$/Mn, respectively. In the intermediate temperature region, TbMn$_2$Si$_2$ makes the new magnetic structure but also have the magnetic phase of low and high temperature region. Such a fact may indicate a severe competition between exchange interaction of Dy-Mn (Antiferromagnetic) and
Mn-Mn (Antiferromagnetic) along the c-axis, and observed in DyMn$_2$Ge$_2$ by Venturini et al$^8$.

Fig. 6 Schematic illustration of the long period structure model of TbMn$_2$Si$_2$ in the temperature between 54.3K and 64.5K.

SUMMARY

The present work reported the results of high resolution powder neutron diffraction studies on TbMn$_2$X$_2$(X:Ge,Si) compounds.

TbMn$_2$Ge$_2$: At the temperature higher than $T_c$=95K, only Mn moments are antiferromagnetically order, where Mn moment is 1.8$\mu_B$/Mn. Below $T_c$, this compound takes simply a collinear ferrimagnetic structure. The value of Tb moment and Mn moment become 9.0$\mu_B$/Tb and 1.8$\mu_B$/Mn, respectively. The magnetic transition below 26K reported by Leciejewicz and Szytula might be concluded in some magnetic state of impurity.

TbMn$_2$Si$_2$: At temperature above 64.5K, only Mn moments order in antiferromagnetically, and the value of Mn moment is 1.8$\mu_B$. Below 54.3K, this compound takes a canted ferrimagnetic structure, where Mn moments make a tilting 42° from the c-axis and Tb moments strongly order ferromagnetically along the c-axis. The value of Tb moment and Mn moment are 9.0$\mu_B$/Tb and 1.8$\mu_B$/Mn, respectively. At intermediate temperature between 54.3K and 64.5K, a new model is proposed, it is a long period structure where is the magnetic cell is compatible with tripling chemical unit cell along the c-axis. In this model, Tb ion, surrounded by the antiferromagnetic net of the Mn moments, could not take any magnetic moment. On the other hand, Tb ion, surrounded by the ferromagnetic net of the Mn moments, could takes full magnetic moment. The moment value are 9.0$\mu_B$ and 1.8$\mu_B$ for Tb and Mn moment, respectively.
ACKNOWLEDGMENTS

The authors would like to thank Messrs. N.Minakawa, Y.Shimoojo, and K.Nemoto for assistance in neutron diffraction experiments.

REFERENCES

P-144

NEUTRON POWDER DIFFRACTION STUDY ON Nd$_2$Fe$_{17}$N$_x$H$_y$ WITH 0 ≤ x < 3.0 AND 0 ≤ y < 1.0

Tsuyoshi KAJITANI, "Yukio MORII, "Satoru FUNAHASHI
"Takahiko IRIYAMA, "Kurima KOBAYASHI, Hiroaki KATO
Yasuaki NAKAGAWA and Kenji HIRAGA

Institute for Materials Research, Tohoku University, Sendai 980.
*Department of Physics, Japan Atomic Energy Research Institute,
Tokai, Ibaragi 319-11.
**Central Laboratory, Asahi Chemical Industry Co. Ltd., Fuji
Shizuoka 416.

ABSTRACT

Present work was aimed to elucidate crystal structure of nitrogenated Th$_2$Zn$_{17}$-type rare-earth metal and iron intermetallic compound hard magnets. For successful neutron diffraction work, neodymium-iron system was chosen. High-resolution neutron powder diffraction measurements with λ=1.8232Å and collimation of 6'-20'-6' on the title compounds were carried out in the temperature range from 13-14K to room temperature. Nitrogenated samples were charged in NH$_3$+H$_2$ mixed gas at 463°C. Coexistence of nitrogen and hydrogen atoms was noticed in the highly gas-charged samples. The maximum nitrogen and hydrogen contents are estimated as N$_{a.0}$ and H$_{a.0}$ per unit chemical formula, Nd$_2$Fe$_{17}$. Nitrogen and hydrogen atoms are located preferentially in 9e(1/2 0 0)-site and 18g(x 2/3 1/6)-site with x~0.2, respectively. The lattice constants-temperature dependencies of the nitrogen/hydrogen free Nd$_2$Fe$_{17}$ exhibited appreciable anomaly below Curie temperature.

INTRODUCTION

Nitrogenated Th$_2$Zn$_{17}$-type rare-earth metal and iron hard magnets, R$_2$Fe$_{17}$N$_x$ with x=3~6 were recently discovered by a Japanese group$^{2-5}$ and a European group$^{4}$'. The highest coercivity 30kOe was achieved by Schnitzke et al.$^{5}$ for the samarium system after the microcrystallization. High Curie temperature at 473°C in Sm$_2$Fe$_{17}$N$_{a.o}$ is one of the advantage for the industrial usages relative to the Nd-Fe-B hard magnet having Tc~320°C$^{7}$. In the samarium system, the Curie temperature increases from about 180°C to up to 473°C by the introduction of interstitial atoms such as carbon$^{8,9}$, hydrogen$^{10,11}$ and nitrogen. The highest Curie temperature was recorded by the nitrogenation$^{2,4}$. The locations and the occupancies of interstitial atoms and magnetic moments of metal atoms in R$_2$Fe$_{17}$X$_y$ with X=C, H(D) and N and y<6 were determined by neutron diffraction$^{9-13}$ and Mossbauer spectroscopy$^{8,14}$. 

--- 455 ---
Nitrogenated praseodymium system was studied in ILL\textsuperscript{12,13} using a high-resolution neutron powder diffractometer. Previously, Jaswal et al.\textsuperscript{14} carried out a medium-resolution neutron powder diffraction study on the nitrogenated neodymium and yttrium compounds. The location sites of the interstitial carbon, hydrogen and nitrogen atoms were assigned at 9e(1/2 0 0)-site and/or 18g(x 2/3 1/6)-site with x \sim 0.2. The 9e-site was only assigned for carbon\textsuperscript{9,10} but both sites were occupied by hydrogen(deuterium) atoms\textsuperscript{10,11}. Though Stalick et al.\textsuperscript{12} and Isnard et al.\textsuperscript{13} reported that the 9e-site was only occupied by nitrogen atoms in the praseodymium system, some controversy\textsuperscript{15} concerning on the site-location of nitrogen atoms in the R\textsubscript{2}Fe\textsubscript{17}N\textsubscript{x} hard magnets remained. Since terminal nitrogen content can be estimated from the location site(s) of nitrogen, it was important to determine them accurately by the use of high-resolution neutron powder diffractometer.

Thermal expansion rate is one of the interesting measure for the magneto-elastic interactions between the magnetic ions either in the magnetically ordered state or short-range ordered state. In the present work, the lattice constants-temperature dependencies were determined for Nd\textsubscript{2}Fe\textsubscript{17}.

EXPERIMENTAL PROCEDURES

The Nd\textsubscript{2}Fe\textsubscript{17} powder sample was prepared from pure neodymium and iron (99.3\%) by induction melting followed by annealing at 1150°C for 40 hours in Ar gas and subsequent pulverization. Nd\textsubscript{2}Fe\textsubscript{17} powder was charged at 465°C in NH\textsubscript{3}+H\textsubscript{2} mixed gas and then dehydrogenated at 465°C in argon gas. The duration of NH\textsubscript{3}+H\textsubscript{2} mixed gas charging was altered from sample to sample in the range from 0.5 hour to 2 hours. Five powder nitrogenated samples plus one nitrogen free sample were prepared. Neutron powder diffraction measurements were carried out in the temperature range from 13K to room temperature using High-Resolution-Powder-Diffractometer constructed in JRR3M reactor hall by Morii et al.\textsuperscript{16} The instrument was operated at \( \lambda =1.8232\)A with collimation of 6'-20'-6' from the first collimator through the third one. Obtained neutron diffraction intensities were analyzed using the Rietveld profile-fitting technique implemented in the program RIETAN\textsuperscript{17}. Colinear ordering of magnetic moments of neodymium and iron atoms parallel to c-plane was assumed. Calculations were carried out based on the (chemical) space symmetry of R\textsuperscript{3}m(No.166). X-ray powder diffraction intensities were measured with CuK\textalpha radiation from room temperature to 520K by the use of PHILIPS-PW1800. Profile-fitting calculation was also applied for the x-ray powder diffraction intensities.

Part of the present work was reported previously\textsuperscript{18}.

RESULTS

Structural Parameters

Figure 1 shows obtained neutron powder diffraction intensities, dots, and their fitted intensities, lines, ofNd\textsubscript{2}Fe\textsubscript{17} and Nd\textsubscript{2}Fe\textsubscript{17}N\textsubscript{3.0} at 13-14K. The profile fitting calculations were performed from 2\( \theta =18\) through 150\( ^\circ \) without "excluded regions". *-signs appeared at about 45\( ^\circ \) in both figures are
due to aluminum sample containers. The sign at about 55° in the Nd$_2$Fe$_{17}$N$_{3.0}$ shows an impurity 220 peak of $\alpha$-Fe precipitated during the nitrogenation. The volume fraction of $\alpha$-Fe was estimated as being less than 0.5 vol%. Agreements between the observed and the fitted intensities are sufficiently good. Bragg peaks appeared in the Nd$_2$Fe$_{17}$ sample shifted toward low scattering angle side in the Nd$_2$Fe$_{17}$N$_{3.0}$, indicating the lattice expansion. The Bragg intensities are also altered by the nitrogenation, e.g. 220 and 303+033 peaks are respectively grown and shrunk in Nd$_2$Fe$_{17}$N$_{3.0}$.

Table I shows obtained structural parameters and magnetic moments. The magnetic components of neutron Bragg reflection were calculated based on the listed form factors, $j_0$, of 4f and 3d electrons of neodymium and iron atoms, respectively. In Nd$_2$Fe$_{17}$N$_{3.0}$, moments of iron atoms are saturated at 13K but the moments are not saturated in Nd$_2$Fe$_{17}$ at 14K. This may indicate that the magnetic structure of Nd$_2$Fe$_{17}$ is slightly different from the c-plane collinear-type at 14K, while that could be the case in Nd$_2$Fe$_{17}$N$_{3.0}$. It is pointed out that the lattice constants of Nd$_2$Fe$_{17}$ show anomalous temperature dependent alteration. The a-axis length decreased with decreasing temperature but c-axis length increased from 12.461Å at room temperature to 12.499Å at 14K, showing strong magnetostricion. On the other hand, the magnetostricion is not noticed in Nd$_2$Fe$_{17}$N$_{3.0}$. 

---
Table I. Structural parameters of Nd$_2$Fe$_{17}$N$_x$ with x=0 & 3 determined by neutron diffraction at room temp. and 13K or 14K.

<table>
<thead>
<tr>
<th></th>
<th>Nd$<em>2$Fe$</em>{17}$</th>
<th>Nd$<em>2$Fe$</em>{17}$</th>
<th>Nd$<em>2$Fe$</em>{17}$Na</th>
<th>Nd$<em>2$Fe$</em>{17}$Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>temp.</td>
<td>14K</td>
<td>R.T.</td>
<td>13K</td>
</tr>
<tr>
<td>Nd</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>6c(0 0 z)</td>
<td>z = 0.3433(10)</td>
<td>0.3420(10)</td>
<td>0.3444(11)</td>
<td>0.3435(9)</td>
</tr>
<tr>
<td></td>
<td>B = 0.33(20)A$^2$</td>
<td>0.02(10)</td>
<td>0.01(32)</td>
<td>0.01(32)</td>
</tr>
<tr>
<td></td>
<td>m = 0.0</td>
<td>3.0(6)</td>
<td>1.8(5)</td>
<td>3.7(3)</td>
</tr>
<tr>
<td>Fe(1)</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>6c(0 0 z)</td>
<td>z = 0.0560(7)</td>
<td>0.0857(8)</td>
<td>0.0944(8)</td>
<td>0.0841(7)</td>
</tr>
<tr>
<td></td>
<td>B = 0.36(8)</td>
<td>0.02(11)</td>
<td>0.47(9)</td>
<td>0.12(11)</td>
</tr>
<tr>
<td></td>
<td>m = 0.6(15)</td>
<td>2.6(6)</td>
<td>2.8(6)</td>
<td>3.0(4)</td>
</tr>
<tr>
<td>Fe(2)</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>9d(1/201/2)</td>
<td>B = 0.36</td>
<td>0.02(11)</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m = 0.0(15)</td>
<td>0.7(5)</td>
<td>1.5(6)</td>
<td>2.4(4)</td>
</tr>
<tr>
<td>Fe(3)</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>18f(x 0 0)</td>
<td>z = 0.2886(7)</td>
<td>0.2904(6)</td>
<td>0.2821(6)</td>
<td>0.2823(6)</td>
</tr>
<tr>
<td></td>
<td>B = 0.36</td>
<td>0.02</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m = 0.5(14)</td>
<td>1.5(4)</td>
<td>1.4(6)</td>
<td>2.2(3)</td>
</tr>
<tr>
<td>Fe(4)</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>18h(x -x z)</td>
<td>z = 0.1669(4)</td>
<td>0.1886(4)</td>
<td>0.1725(5)</td>
<td>0.1722(4)</td>
</tr>
<tr>
<td></td>
<td>B = 0.32</td>
<td>0.02</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m = 0.1(14)</td>
<td>1.4(4)</td>
<td>1.8(4)</td>
<td>2.5(3)</td>
</tr>
<tr>
<td>N</td>
<td>occ. = 1.0</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9e(1/2 0 0)</td>
<td></td>
<td>0.95(4)</td>
<td>1.00(2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>m = 0.0(15)</td>
<td>0.46(29)</td>
<td>0.20(15)</td>
<td></td>
</tr>
</tbody>
</table>

Structural refinement calculations were repeated to find proper nitrogen location(s). It is concluded that nitrogen atoms mainly occupy 9e(1/2 0 0)-site. The occupancy at 18g(x 2/3 1/6)-site could be possible but very limited, about less than 1% in the present neodymium system. There were different interstitial atoms which have negative scattering length in three heavily charged samples. Possible candidate of the interstitial atoms is hydrogen which was charged during the nitrogenation process. High hydrogen content, H$_2$-es, was concluded in one of the highly charged samples. In the same sample, nitrogen content was N$_2$-es per unit chemical formula, Nd$_2$Fe$_{17}$.

Total magnetic moment, i.e. the summation of determined magnetic moments of metallic atoms, in the hydro-nitrogenated Nd$_2$Fe$_{17}$N$_{2.88}$H$_{0.58}$ is 30.2$\mu$$_B$ at room temperature. This moment is lower than the value 37.6$\mu$$_B$ of Nd$_2$Fe$_{17}$Na$_{0.8}$, measured by the extrapolation experiments done in high magnetic field up to 25 Tesla by Iriyama et al.\textsuperscript{20}. It may be suggested that interstitial hydrogen atoms decrease the total magnetic moment of the
charged samples.

Anomalous Thermal Expansion

Figure 2 shows lattice constants-temperature dependencies of a- and c-axes and unit cell volume measured by neutron (from room temperature to 13-14K) and x-ray (from room temperature to 520K) diffractions. The error ranges of the determined lattice constants are included in the circles. Very strong spontaneous magnetostriction is observed parallel to the c-axis below 400K where the system becomes ferromagnetic. Non-linear lattice expansion parallel to the a-axis is also noticed below 400K. Similar spontaneous magnetostriction in Y$_2$Fe$_{17}$ was reported by Givord and Lemaire$^{11}$. The c-axis of Y$_2$Fe$_{17}$ was elongated at temperatures below Curie temperature down to the liquid He temperature. Givord and Lemaire found that the Fe-Fe

---

**Table II.** Intertatomic distances (Å) between nearest atoms in Nd$_3$Fe$_{17}$N$_x$ with x=0 and 3 at room temp. and at 13K or 14K.

<table>
<thead>
<tr>
<th>atom pairs</th>
<th>Nd$<em>3$Fe$</em>{17}$</th>
<th>Nd$<em>3$Fe$</em>{17}$</th>
<th>Nd$<em>3$Fe$</em>{17}$N$_3$</th>
<th>Nd$<em>3$Fe$</em>{17}$N$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>temp.</td>
<td>R.T.</td>
<td>14K</td>
<td>R.T.</td>
<td>13K</td>
</tr>
<tr>
<td>Nd - Fe(1)c</td>
<td>3.082(21)</td>
<td>3.078(22)</td>
<td>3.164(24)</td>
<td>3.149(20)</td>
</tr>
<tr>
<td>Nd - Fe(2)d</td>
<td>3.313(12)</td>
<td>3.308(12)</td>
<td>3.388(14)</td>
<td>3.373(11)</td>
</tr>
<tr>
<td>Nd - Fe(3)f</td>
<td>3.073(15)</td>
<td>3.059(14)</td>
<td>3.177(17)</td>
<td>3.171(13)</td>
</tr>
<tr>
<td>Nd - Fe(4)h</td>
<td>3.105(20)</td>
<td>3.119(18)</td>
<td>3.174(22)</td>
<td>3.175(18)</td>
</tr>
<tr>
<td>Fe(1)c-Fe(1)c</td>
<td>2.335(17)</td>
<td>2.392(20)</td>
<td>2.380(20)</td>
<td>2.379(19)</td>
</tr>
<tr>
<td>Fe(1)c-Fe(2)d</td>
<td>2.028(9)</td>
<td>2.628(10)</td>
<td>2.689(10)</td>
<td>2.745(10)</td>
</tr>
<tr>
<td>Fe(1)c-Fe(3)f</td>
<td>2.748(11)</td>
<td>2.761(11)</td>
<td>2.749(11)</td>
<td>2.745(10)</td>
</tr>
<tr>
<td>Fe(1)c-Fe(4)h</td>
<td>2.640(10)</td>
<td>2.642(10)</td>
<td>2.678(12)</td>
<td>2.679(7)</td>
</tr>
<tr>
<td>Fe(2)d-Fe(3)f</td>
<td>2.440(8)</td>
<td>2.312(6)</td>
<td>2.477(5)</td>
<td>2.333(5)</td>
</tr>
<tr>
<td>Fe(2)d-Fe(4)h</td>
<td>2.460(9)</td>
<td>2.462(6)</td>
<td>2.496(10)</td>
<td>2.495(8)</td>
</tr>
<tr>
<td>Fe(3)f-Fe(3)f</td>
<td>2.474(5)</td>
<td>2.489(5)</td>
<td>2.475(5)</td>
<td>2.473(6)</td>
</tr>
<tr>
<td>Fe(3)f-Fe(4)h</td>
<td>2.971(12)</td>
<td>2.923(6)</td>
<td>2.998(12)</td>
<td>3.041(4)</td>
</tr>
<tr>
<td>Fe(4)h-Fe(4)h</td>
<td>2.522(9)</td>
<td>2.513(7)</td>
<td>2.646(10)</td>
<td>2.637(7)</td>
</tr>
<tr>
<td>N(1) - Nd</td>
<td>(2.479(12))</td>
<td>(2.476(1))</td>
<td>2.537(14)</td>
<td>2.533(1)</td>
</tr>
<tr>
<td>N(1) - Fe(3)f</td>
<td>(1.815(8))</td>
<td>(1.796(5))</td>
<td>1.912(5)</td>
<td>1.907(5)</td>
</tr>
<tr>
<td>N(1) - Fe(4)h</td>
<td>(1.059(7))</td>
<td>(1.970(10))</td>
<td>1.930(8)</td>
<td>1.933(5)</td>
</tr>
</tbody>
</table>
interatomic distances below 2.44Å at room temperature decreased in the low temperature range but the Fe-Fe distances beyond 2.44Å increased. That was partly the case in the Nd$_2$Fe$_{17}$. Table II shows interatomic distances between nearest atoms in Nd$_2$Fe$_{17}$N$_x$ with x=0 and 3 at room temperature and at 13-14K. Fe(1)-Fe(1), Fe(2)-Fe(3) and Fe(2)-Fe(4) distances being shorter than 2.44Å decreased at 14K. Significant decrease in the Fe(2)-Fe(3) distance from 2.44Å to 2.31Å is noticed. Other interatomic distances, except Fe(4)-Fe(4) distance, altered positively or kept nearly constant at 14K. On the other hand, above mentioned Givord and Lemaire's criterion in the interatomic distances at 2.44Å could be increased up to 2.75Å in the nitrogenated sample, Nd$_2$Fe$_{17}$N$_{3.0}$. Fe(1)-Fe(1), Fe(2)-Fe(3), Fe(2)-Fe(4), Fe(3)-Fe(3) and Fe(4)-Fe(4) interatomic distances, being shorter than 2.75Å at room temperature, decreased at 13K. Exceptional increase from 2.69Å to 2.76Å was recorded for Fe(1)-Fe(2) distance, however.

DISCUSSIONS AND CONCLUSIONS

Detailed structural study was carried out for the gas uncharged as well as charged Nd$_2$Fe$_{17}$ at temperatures from 13-14K to room temperature by the use of a high resolution neutron diffractometer JRR3M-HPD. Location sites and their occupancies of charged nitrogen and hydrogen atoms, magnetic moments of metallic atoms and lattice constants of uncharged and five charged Nd$_2$Fe$_{17}$ samples were determined by means of Rietveld profile fitting technique.

As expected, the maximum nitrogen content of the charged sample was N$_{3.0}$ per unit chemical formula. Nitrogen atoms were almost only located at 9e(1/2 0 0)-site. Occupancy of nitrogen atoms at 18g(x 2/3 1/6)-site with x~0.2 was less than the meaningful level. The 18g(x 2/3 1/6)-site was partly occupied by hydrogen atoms in the highly charged samples which were hydro-nitrogenated. The maximum occupancy of hydrogen atoms at 18g-site was less than 1/6 in the hydro-nitrogenated Nd$_2$Fe$_{17}$. Six 18g-sites form a six-member ring, where each 18g-site is separated about 1.32Å. Possible full occupancy of the 18g-site must be 1/3 or less, i.e. only two hydrogen atoms can situate in one ring because of the Westlake's criterion$^{22}$ for the minimum stable H-H distance at 2.1Å allowed in the hydrogenated metals. Since observed maximum occupancy at 18g-site was less than 1/6, nitrogenation of Nd$_2$Fe$_{17}$ could lower the hydrogen solubility there.
Figure 3 shows a crystal structure of Nd$_2$Fe$_{17}$N$_2.28$Ho$_{0.93}$ drawn based on the determined structure parameters. Nitrogen atoms are at the center of a- and b-axes. Six hydrogen sites forming a six-member ring are located between two neodymium atoms. Since observed maximum hydrogen occupancy at the hydrogen site is 0.15, that is, less than 1/6, only one of the six sites is occupied in the nitrogenated Nd$_2$Fe$_{17}$. The total magnetic moment of the samples increases by the nitrogenation, but decreases by the further gas, i.e. hydrogen, charging.

Temperature dependencies in the structural parameters were carefully studied. Well defined spontaneous magnetostriction is found in Nd$_2$Fe$_{17}$ sample parallel to the c-axis. The temperature dependency in the a-axis length is also non-linear in the ferromagnetic state. Fe-Fe interatomic distances shorter than 2.44Å at room temperature are shortened at 13K, showing similarity to Y$_2$Fe$_{17}$. Strong magnetic interaction between Fe(3)-Fe(4) pair separated by 2.68Å, which is longer than 2.44Å, exists in Nd$_2$Fe$_{17}$, however. Strong coupling between "ring"-sites ions, Fe(2)-Fe(3), is also noticed. Such interaction causes spontaneous magnetostriction. On the other hand, positive magnetic interactions between iron atoms seem to be enhanced by the nitrogenation. Fe-Fe pairs separated by the distances less than 2.75Å at room temperature become shorter appreciably at 13K in Nd$_2$Fe$_{17}$N$_{0.9}$, in which strong spontaneous magnetostriction did not exist.

Further work is underway to determine the temperature dependencies in the lattice constants of samarium compounds. Similar spontaneous magnetostriction is observed in Sm$_2$Fe$_{17}$ in which anomalous lattice expansion is noticed in the c-plane just below the Curie temperature. These results will be reported separately.$^{23}$

ACKNOWLEDGMENT

Sincere and kind technical assistances for the present neutron diffraction work by Messrs. Y. Shimojo and N. Minakawa are gratefully appreciated. Support by the Department of Research Reactor of JAERI is acknowledged.
REFERENCES

20. T. Iriyama, H. Kato and Y. Nakagawa (private comm.).
23. T. Kajitani, H. Shishido and K. Hiraga; to be published.
INCOHERENT NEUTRON SCATTERING OF HYDROGEN BOND COMPOUNDS
I. EXPERIMENTS AT STEADY REACTOR

*Yukio NODA, *Itaru TAMURA, *Susumu IKEDA and
#Yasusada YAMADA

*Faculty of Science, Chiba University,
Yayoi, Chiba 263, Japan

*KENS, National Laboratory
for High Energy Physics,
Tsukuba 305, Japan

#A Professor Emeritus, Osaka University,
Toyonaka, Osaka 560, Japan

ABSTRACT

Incoherent neutron scattering experiments of KH$_2$PO$_4$ and
K$_3$H(SO$_4$)$_2$ were performed in order to study the role of the
hydrogen dynamics for the isotope effect in hydrogen bond
materials. Experiments were carried out under the collaboration
between the pulse neutron source(KENS) and the steady reactor
source(JRR-3M), and this paper will report the part of the ex-
perimental results taken at JRR-3M. Precise temperature depen-
donences of elastic and inelastic incoherent neutron scattering were
measured. The elastic scattering of KH$_2$PO$_4$ along $a$-direction
apparently increased and the inelastic component decreased at $T_c$.
The Q-dependence of the change at $T_c$ of the elastic intensity as
well as that of inelastic intensity at $\Delta E = 5$ meV show a broad peak
around 5 to 7 Å$^{-1}$. The analysis of inelastic scattering profiles
gives the extraordinary broad width. Even when the existence of
the tunneling mode is assumed, the characteristic energy is 1.1 meV
and the width(FWHM) is 24 meV, which is different from the assumed
tunneling state. Thus, the motion of hydrogen atoms seems to have
a stochastic character. The incoherent scattering profile of
K$_3$H(SO$_4$)$_2$ shows an inelastic component but no drastic change was
observed as a function of temperature since this compound has no
phase transition temperature. These results are completely con-
sistent with the results given by the pulse neutron experiments.

INTRODUCTION

The isotope effect in the hydrogen-bonded system (large shift
of the transition temperature upon isotopic replacement of
hydrogen by deuteron) has been one of the 'time-honored' problems
in solid state physics. Since the tunneling mode model was
proposed, a few decades have passed without any concrete evidence
of the existence of proton tunneling mode relevant to the phase
transitions in hydrogen bonded materials.
KH₂PO₄, abbreviated as KDP, is one of the most extensively studied materials. KDP undergoes a ferroelectric phase transition at 123K, where the transition temperature of deuterium compound KD₂PO₄ is 232K. The proton motion on the hydrogen bonds, forming the network along the a- and the b- axis of the tetragonal system, is considered to be relevant to cause the phase transition. Another example is provided by K₃H(SO₄)₂, abbreviated as K₃HS. The crystal has a very simple structure in which the hydrogen bonds are isolated instead of forming the network. The isotope effect of this system is extraordinary: The transition temperature of deuterium compound is 84K while that of hydrogen compound is considered to be below zero kelvin. That is, the hydrogen compound does not undergo the phase transition. Nevertheless, the proton density distribution is observed to exhibit a double peak structure above 100K, which changes gradually to a single peak feature as the temperature is decreased.1)

In order to study the motion of hydrogen atoms, the measurement of incoherent neutron scattering provides a powerful technique since the incoherent scattering cross section of hydrogen nucleus is overwhelmingly large. Further, incoherent scattering gives the information of the individual hydrogen motion.

EXPERIMENTAL

A single crystal of KDP and a polycrystalline of K₃HS partially oriented along c*-direction were used. Experiments were carried out under the collaboration between the pulse neutron source(KENS, KEK) and the steady reactor source(JRR-3M, JAERI), and this paper will report the part of the experimental results taken at JRR-3M.

Triple axis spectrometers(GPTAS and PONTA) were used to measure the elastic and inelastic incoherent neutron scattering. Incident energies and collimations were changed depend on the experimental conditions: 30.5, 40, 70 and 150meV were used as an incident energy with PG002 or Cu220 monochrometer. PG002 or PG004 as an analyzer was used with PG-filter. The sample was installed in CTI refrigerator cryostat, and the temperature was controlled within 0.1K.

RESULTS AND ANALYSIS

Experiments of KDP

Elastic scattering along a* and c* directions are shown in Fig.1 as a function of momentum transfer Q. The data at 300K and 150K shown in the figure are above Tc and those at 100K and 20K are below Tc. The intensities show monotonous decrease and extra structures such as shoulder peaks are not seen. The intensity distribution changes abruptly at Tc as shown in the same figure. The difference of intensities between 150K and 100K gives a broad peak around 5 to 7 Å⁻¹.

The energy spectra were also measured at various Q-values. As an example, scattering profiles taken at Q=7Å⁻¹ are shown in Fig.2. Besides the elastic component, considerably strong
quasielastic intensity is observed extending over a large range of the energy transfer. When the temperature is decreased, the elastic intensity increases at the expense of the inelastic component. The temperature dependences of elastic and inelastic intensities are shown in Fig. 3. Apparently, sudden change appears at the transition temperature Tc. Therefor, we conclude that the hydrogen motion is frozen at Tc and the inelastic intensity is transferred to the elastic part which reflects a static structure. The intensity distribution at ΔE = 5meV is also measured as a function of momentum transfer Q, as shown in Fig. 4. Again, it shows a broad peak at 5 to 6 Å⁻¹.

The quasielastic scattering shown in Fig. 2 is analyzed by two kinds of trial functions. One is two Gaussian peaks centered at characteristics energy ± 8 o, and the other is a single Lorentzian peak at energy zero. The tunneling

---

Fig. 1
Elastic incoherent scattering from KDP as a function of momentum transfer Q.

---

Fig. 2
Inelastic scattering profile at Q=7Å⁻¹
model corresponds to the two Gaussian function analysis. Both analyses gave almost the same fitting curve. The obtained best fit parameters $\sigma$ and its width (FWHM) in two Gaussian model are 1.1meV and 24meV, respectively. These numbers are obviously far from the assumed tunneling state. The parameter in a single Lorentzian peak model give the width (FWHM) 21meV, which is considerably large to be interpreted by the ordinary relaxation process over a potential barrier.

Experiments of $\text{K}_3\text{MnS}$

The elastic and inelastic incoherent scattering intensities were observed at various temperatures and various $Q$ values. Shown in Fig.5 is the scattering profile taken at $Q=5\text{Å}^{-1}$ perpendicular to the c* direction. At high temperature, broad inelastic intensity was observed. There seems to exist an inelastic peak at around 7meV. Upon cooling, the peak at 7meV becomes clearer. Precise temperature dependence of elastic and inelastic intensities were measured in order to clarify the change of nature of the hydrogen motion corresponding to the change from two peak feature to a single peak feature of hydrogen distribution. However, we could not observe any appreciable temperature dependence in elastic and inelastic intensities.
compared with the KDP case as shown in Fig. 3. In Fig.6, the Q-dependences of inelastic intensities at 3.5meV and 7meV at 250K and 10K are shown.

Fig.5
Inelastic scattering of K\textsubscript{3}HS at Q=5\textsubscript{\AA}^{-1}.

SUMMARY AND DISCUSSIONS

We have measured incoherent neutron scattering from KDP and K\textsubscript{3}HS. Remarkable change of elastic and inelastic intensities were observed at the phase transition temperature of KDP. The analysis of the energy profile based on proton tunneling mode model gives unrealistic parameter value for the tunneling frequency. On the other hand, the analysis based on random hopping model also gives unreasonable parameter value for the hopping relaxation time. An alternative model and the analysis of the neutron incoherent scattering based on the new model will be given elsewhere.

Fig.6
Q-dependence of inelastic intensity of 3.5meV and 7meV at 250K and 10K.

REFERENCE

STRUCTURE OF MARTENSITIC PHASE AND PHONON INSTABILITY IN Cu$_{61}$Zn$_{39}$

*Akio KONISHI, **Yoshihiro KUROWA, *Yukio NODA, **Kazuhiko FUCHIZAKI,
+Satoru FUNAHASHI, +Susumu KATANO, **H. R. CHILD,
#Henry CHOU, ##Yasusada YAMADA and ###S. C. MOSS

*Faculty of Science, Chiba University, Yayoi, Chiba 263, Japan
**Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812, Japan
+Solid State Physics, Tokai Research Establishment, JAERI
Tokai, Ibaraki 319-11, Japan
**Oak Ridge National Laboratory, Oak Ridge, TN 37831, U.S.A.
#Brookhaven National Laboratory, Upton, N.Y. 11973 U.S.A.
##A Professor Emeritus, Osaka University, Toyonaka, Osaka 560, Japan
###Dept. of Physics, University of Houston, Houston, TX 77004, U.S.A.

ABSTRACT

In order to study the mechanism of the martensitic phase transformation in Cu$_{61}$Zn$_{39}$, neutron elastic and inelastic scattering experiments were performed at JRR-2 and JRR-3M of JAERI and HFIR of Oak Ridge National Laboratory. Measurements of phonon dispersion curve indicate that the entire TA$_2$[110] phonon mode is extremely soft and shows further softening on decreasing temperature. However, no anomalies in dispersion relations found in other directions studied. The structure of the martensite phase was investigated by using a WAND spectrometer on (HHL) and (HEO) planes. Analysis of two-dimensional intensity data indicates that the structure of martensite phase in Cu$_{61}$Zn$_{39}$ is slightly different from the 9R* structure reported by Tadaki et al.. We propose a mixed phase of a distorted CsCl structure and a three-period lattice as the structure of martensite phase.

INTRODUCTION

A $\beta$-brass CuZn alloy is well-known to exhibit so-called shape memory effect which is associated with the thermoelastic martensitic phase transformation. The thermoelastic martensite transformation is investigated experimentally and theoretically based on a phonon instability. In low temperature phase, $\beta$-type martensite alloys have long period stacking structures called 2H, 9R or 7M. For example, $\beta$-Au-Cu-Zn, $\beta$-Cu-Al-Ni and NiAl alloys have 9R, 2H and 7M structures respectively[1-3]. In these alloys, anomalous dip in the phonon dispersion curve and diffuse scattering were observed above transition temperature. In Ni$_2$GaAl$_2$Ga$_3$, for example, the phonon dispersion curve shows a dip near $q=(1/7)[110]$ position of the TA$_2$[110] (e=[110]) phonon mode, and diffuse scatterings appear near $q=(1/7)[110]$.
position\(^4\). In Au-Cu-Zn alloy, on the other hand, there is a dip near \(q=1/3\)[110] position of the \(TA_2[110]\) mode, which is accompanied by a diffuse scattering at around the position giving rise to the dip\(^5\). These phenomena are understood as manifestation of lattice instabilities inherent in \(\beta\) (bcc) structure.

In CuZn alloy, early experiments indicated that the structure of martensite phase was 9R structure constructed by the shift of \(\langle 110\rangle\) planes with \(\langle 210\rangle\) stacking sequence. In this case, the magnitude of shift \(\Delta u\) of each \(\langle 110\rangle\) plane is 1/6, and the resultant 9R structure is orthorhombic structure. However, Tadaki et al. reported that the structure of martensite phase in Cu\(_{60}\)Zn\(_{40}\) is monoclinic 9R' structure and a shift \(\Delta u\) is 0.146 slightly different from 1/6.

In this study, we investigate phonon instability and the structure of martensite phase in Cu\(_{61}\)Zn\(_{39}\) alloy which has a concentration close to the above alloy, in order to elucidate the transformation mechanism from \(\beta\) to monoclinic 9R' structure.

**EXPERIMENTS**

A single crystal of Cu\(_{61}\)Zn\(_{39}\) was used in this experiment. It was approximately cylindrical (15 mm diameter and 30 mm height) in shape. In order to determine the transition temperature of this particular sample, the measurement of the intensity of the superlattice reflection was performed by triple-axes neutron spectrometer (TANSI) at JRR-2 of JAERI. The energies of incident neutron used were 30.5 meV and 13.7 meV, and collimation of 60°-40°-40°-60° was used. As a result, superlattice reflections appeared at \(q=1/3\) in the [110] direction were observed. As an example, the temperature dependence of a \((7/3, -1/3, 0)\) reflection is shown in Fig. 1. The new bragg reflection appeared at 125K upon decreasing temperature, and the reflection disappeared at 135K upon increasing temperature. Therefore, the transition temperature is determined as \(T_s=125K\). The distribution of scattering intensity along the [110] direction above the transition temperature is shown in Fig. 2. Not only the diffuse streak along [110] direction, the diffuse scatterings appear at \(q=1/3\)[110] and at \(q=1/6\)[110] positions, and the latter particularly shows large temperature dependence compared with the former. In addition, the latter is at the position that has no relation to \(\beta\) R' structure. Considering
these points, there is the possibility that phonon instability exists at \( q = (1/3)[110] \) position or at \( q = (1/6)[110] \) position.

The measurement of phonon dispersion curve was performed by triple-axes neutron spectrometer (TAS-1 and TAS-2) at JRR-3M of JAERI. Both constant-Q scan and constant-E scan, with fixed incident neutron energy \( E_i \), were used to measure the phonon spectra. \( E_i \) used in the measurement was 40.8meV and 30.0meV at TAS-1, and 13.8meV at TAS-2. Collimations of 40'-40'-40'-40' and 20'-20'-20'-20' at TAS-1, and 20'-20'-20'-20' at TAS-2 were used. The measurements of phonon dispersion curve were performed in [100], [110], [111] and [112] directions at room temperature, and the measurement of TA\(_2[110]\) phonon mode was also performed at 140K just above \( M_s \).

In order to investigate the structure of martensite phase in Cu\(_6\)Zn\(_{53}\), we used a WAND spectrometer in HFIR of Oak Ridge National Laboratory. Wide angle proportional counter is equipped with the WAND, so that we can quickly look into wide region in reciprocal space by changing crystal angle. The instability distributions on (HKL) plane and (HHL) plane were measured at 300K, 145K and 12K.

**RESULTS AND ANALYSIS**

1. Phonon dispersion relation

The observed phonon dispersion curve is shown in Fig. 3(a). In this figure, open circles are the phonon energies at room temperature, and triangles are those at 140K. Observed scattered profiles are normal except several points indicated by cross-marks in the figure. At those points, anomalous double-peak feature in the scattered profiles is observed in the TA\(_1[110]\) phonon and TA[111] phonon as is shown in Fig. 4. The similar feature has also been observed in ZrNb alloy\(^{(7)}\). It is shown \(^{(8)}\) that the origin of this anomaly can be ascribed to long-lived heterogeneous fluctuations occurred in highly anharmonic lattice vibrations. It is therefore inferred that double-peak feature observed in this alloy may be attributed to the anharmonic nature of a \( \beta \)-structure.

![Fig. 3(a)](image)

**Fig. 3(a)** The observed phonon dispersion curve in Cu\(_6\)Zn\(_{53}\). Open circles are the phonon energies at room temperature, and triangles are those at 140K. Cross marks indicate the position that anomalous scattering profiles are observed. The entire TA\(_2[110]\) is extremely soft and shows softening on decreasing temperature.

![Fig. 3(b)](image)

**Fig. 3(b)** The calculated phonon dispersion relation based on a simple lattice dynamics which consider the interactions of the atoms within the second nearest neighbor.
From Fig. 3, we easily observe that the entire \( TA_{2}[110] \) phonon mode \((\mathbf{q} \parallel [110], \mathbf{e} \parallel [110])\) is considerably soft, and shows further softening upon increasing temperature as is seen generally in martensite alloys. However, no anomalous dip is shown at \( \mathbf{q} = (1/8)[110] \) or \( \mathbf{q} = (1/3)[110] \) where diffuse scatterings appear. This behavior is apparently different from those observed in NiAl, Au-Cu-Zn and Cu-Al-Ni alloys. In this context, there is no evidence of the softening of the relevant phonon with a particular \( \mathbf{q} \)-vector as the origin of the martensite transformation.

In order to discuss whether or not the elastic constants of the Cu66Zn33 alloy is normal, we derived sound velocities from the initial slope of the observed acoustic phonon modes, and elastic constants were calculated. The observed sound velocity and elastic constants are depicted in Table 1. There are only three elastic constants in a cubic system: \( C_{11}, C_{12} \) and \( C_{44} \). By solving the equations of force balance acting on each atom in the crystal, effective elastic constants for each direction are obtained and given in Table 1. The elastic constants: \( C_{11}, C_{12} \) and \( C_{44} \) were calculated from the \( LA[100] \), \( TA_{2}[110] \) and \( TA[100] \) phonon modes, respectively, and the elastic constants of other directions were calculated by using these three elastic constants. Comparing the observed elastic constants with the calculated ones, we conclude that the elastic constants for each direction are normal.

<table>
<thead>
<tr>
<th>( \mathbf{q} )</th>
<th>( \mathbf{e} )</th>
<th>velocity</th>
<th>( v_{ob} )</th>
<th>Elastic constant</th>
<th>( C_{ob} )</th>
<th>( C_{calc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA[100]</td>
<td>[100]</td>
<td>( \sqrt{C_{11}} )</td>
<td>4.2</td>
<td>( C_{11} )</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>TA[100]</td>
<td>[010]</td>
<td>( \sqrt{C_{44}} )</td>
<td>2.9</td>
<td>( C_{44} )</td>
<td>7.0</td>
<td>-</td>
</tr>
<tr>
<td>LA[110]</td>
<td>[110]</td>
<td>( \sqrt{C_{11} + C_{12} + 2C_{44}} )</td>
<td>4.7</td>
<td>( \frac{1}{2}(C_{11} + C_{12} + 2C_{44}) )</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td>TA[110]</td>
<td>[001]</td>
<td>( \sqrt{C_{11}} )</td>
<td>2.9</td>
<td>( C_{44} )</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>TA[110]</td>
<td>[110]</td>
<td>( \sqrt{C_{11} - C_{12}} )</td>
<td>0.85</td>
<td>( \frac{1}{2}(C_{11} - C_{12}) )</td>
<td>0.61</td>
<td>-</td>
</tr>
<tr>
<td>LA[111]</td>
<td>[111]</td>
<td>( \sqrt{C_{11} + 2C_{12} + 4C_{44}} )</td>
<td>5.7</td>
<td>( \frac{1}{2}(C_{11} + 2C_{12} + 2C_{44}) )</td>
<td>27</td>
<td>24</td>
</tr>
<tr>
<td>TA[111]</td>
<td>[110]</td>
<td>( \sqrt{C_{11} - C_{12} + 2C_{44}} )</td>
<td>1.8</td>
<td>( \frac{1}{3}(C_{11} - C_{12} + 2C_{44}) )</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>LA[112] ( \approx [112] )</td>
<td>( \sqrt{C_{12}} )</td>
<td>4.8</td>
<td>( \frac{1}{2}C_{4} )</td>
<td>19</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>TA[112] ( \approx [111] )</td>
<td>( \sqrt{C_{44}} )</td>
<td>1.4</td>
<td>( \frac{1}{3}C_{4} )</td>
<td>16</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>TA[110] ( \approx [110] )</td>
<td>( \sqrt{C_{11} - C_{12} + 2C_{44}} )</td>
<td>-</td>
<td>( \frac{1}{3}(C_{11} - C_{12} + 2C_{44}) )</td>
<td>4.9</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 The sound velocities and the elastic constants for each direction. The elastic constants; \( C_{11}, C_{12}, \) and \( C_{44} \) were calculated from the \( LA[100], TA_{2}[110] \) and \( TA[100] \) phonon modes, respectively, and the elastic constants of other directions were calculated by using these three elastic constants. In this table, the elastic constants for [112] direction: \( C_{4} \) and \( C_{6} \) are given as follows:

\[
C_{4} = \frac{1}{12}(5C_{11} + C_{12} + 8C_{44}) \pm \left( (3C_{11} - C_{12} - 4C_{44})^{2} + 32(C_{12} + C_{44})^{2} \right)^{\frac{1}{2}}
\]
As the next stage, we study whether the whole behavior of lattice vibration is normal. Phonon dispersion relations are calculated based on a simple lattice dynamics in which the interactions of the atoms within the second nearest neighbor are taken into account. The calculated dispersion relations are shown in Fig. 3(b). As shown in the figure, the calculated curves give a good agreement with the observed ones. Therefore, it seems that the behavior of the lattice vibration does not show any anomalies.

2. Structure of martensite phase

Fig. 5 shows the intensity distribution on (HK0) plane in the reciprocal space obtained by the WAND spectrometer. The intensity map in Fig. 5(a) is taken at room temperature, and that of Fig. 5(b) is taken at 12K. At room temperature, the Bragg reflections of the CsCl structure are observed, while many Bragg reflections which are originated from a structure of the martensite phase and its domains are observed at 12K. By analysing the positions of Bragg reflections at 12K, we investigate the structure of martensite phase as follows.

First, we compared the observed Bragg reflection with the reciprocal lattice of a 3M structure, as shown in Fig. 6. Here, the 3M structure is essentially equivalent to the 9R' structure reported by Tadaki et al. It is seen that the positions of the observed Bragg reflection do not agree with the reciprocal lattice points of the 3M structure. In order to account for the distribution of the Bragg reflections, we propose that the specimen is in a mixed phase composed of two structures. One of the structure is an orthorombic structure which is distorted from the original CsCl structure, and the other is a monoclinic structure which has a unit cell tripled along the [110] direction of the CsCl structure as shown in Fig. 7. Note, however, this monoclinic structure seems to be somehow different from above 3M structure. If we apply the (21) stacking sequence like the 9R' structure to this three-period lattice, the third layer of (110) plane in the
CsCl structure should not shift from the initial position, because the magnitude of the $\beta$ angle in this three-period structure is very close to the value in $\beta^*$ structure when the magnitude of the shift $\Delta u$ is zero. This means that the assumed (21) stacking sequence is not applicable to this martensite phase.

Concerning the observed (HK0) plane, almost all reflections observed were explained by adopting the mixed phase structures with a few exceptions. But, concerning the observed (HHL) plane, there are still unsolved domain structures. For instance, the crystal axis of some domains which explain the reflection on (HHL) plane deviates considerably from the original cubic axis. At the present stage, it is not clear whether these domains really exist or not. It is necessary to investigate the domain structure more precisely in the three dimensional reciprocal space.

**SUMMARY**

We investigate phonon instability and the structure of martensite phase in Cu$_5$Zn$_3$. The entire TA$_2(\bar{1}10)$ phonon mode is considerably soft, and shows softening on decreasing temperature. Diffuse scatterings were observed as the precursor phenomena. However, no anomalous behavior of phonon is observed at the wave numbers which give rise to those diffuse scatterings. We can not give at the moment a clear explanation about the relationship between diffuse scatterings and the phonon instability observed in the CuZn alloy. We analyzed the structure of martensite phase, and found that the structure was not explained by the SM structure reported by Tadaki et al. Observed distribution of Bragg intensities are explained by assuming two structures coexisting in the sample. The one is an orthorombic structure which is distorted from the original CsCl structure, and the other is the three-period monoclinic structure.

**REFERENCES**

MAGNETIC STRUCTURE OF ITINERANT ELECTRON ANTIFERROMAGNETS Mn_{3-x}T_xSi (T=Cr,Fe)

Hiroyuki Miki, Kenji Ohoyama, Satoru Funahashi*, Shoichi Tomiyoshi**, Yasuo Yamaguchi

Institute for Materials Research, Tohoku University, Sendai 980

*JAERI, Tokai, Ibaraki 319-11

**Faculty of Engineering, Ehime University, Matsuyama 790

ABSTRACT

Magnetic and crystallographic structures of Mn_{3-x}T_xSi (T=Cr,Fe) system are studied by means of X-ray and neutron diffraction measurements. The results indicate that all these alloys crystallize to the L2_1 (Heusler) structure and show antiferromagnetic properties. Using the nuclear scattering data, the site preference of substituted elements (T) is obtained that Cr enters predominantly the site with eight Mn first near neighbors and Fe enters the other site which has four Mn and four Si first near neighbors. The values of magnetic moment were calculated Tomiyoshi model, which assumed the transversal sinusoidal spin ordering with the wave vector q being parallel to the [111] axis. From this model we conclude the structure that the magnetic moments are in the (111) plane, except for y=1.2 that is along the [111] direction. Incommensurate spin density wave is observed to be stable for the concentration range of 0≤x≤0.1 and 0≤y≤0.1.

INTRODUCTION

Mn_3Si is an itinerant-electron antiferromagnet with the transversal sinusoidal spin structure. The magnetic properties of Mn_3Si including magnetic excitations are interesting in comparison with a typical itinerant antiferromagnet bcc Cr, which shows the spin density wave. The spin wave in Mn_3Si has a linear dispersion with a fairly high slope at lower energy. The two dispersion cones emanating from a pair of satellite Bragg points interact with each other, and after that the magnetic excitations change drastically from that expected from the lower part. In spite of these interesting property, there was no systematic work on Mn_3Si until now. Crystal structure is shown in Fig.1.

In the present study we have examined the alloying effect on the magnetism of Mn_3Si. We made samples of Mn_{3-x}Cr_xSi and Mn_{3-y}Fe_ySi, and have carried out X-ray
and neutron diffraction measurements on these samples.

EXPERIMENTAL DETAILS

The alloys were prepared from stoichiometric mixtures of the constituent elements and melted in an argon arc furnace into a series of alloy buttons. Then the samples were powdered and sealed into an evacuated quartz ampoules, and annealed for 7 days at 900 °C to ensure homogeneity. The ampoules were cooled slowly to the room temperature.

X-ray diffraction pattern using Fe Kα radiation was obtained for each sample at room temperature. Single phase substances with clear superlattice lines of the D0₃ (Fe₃Al-type) structure were obtained for alloys with Cr, but samples of Fe substitution contained a second phase, though its amount was negligibly small.

The neutron diffraction measurements were performed using the spectrometers of TAS-2, KSD and KPD installed in JRR-3 reactor of JAERI. Results are shown in Fig.2.

RESULTS AND DISCUSSION

The X-ray diffraction measurements of the samples showed that the single phase region of the cubic D0₃-type crystal structure is 0<x<0.25 for Cr substitution and whole range of Fe substitution. In the present investigation we prepared the samples of 0<x<0.2 and 0<y<1.2.

For the Mn₃₋ₓFeₓSi system, lattice parameter decrease linearly from 5.72 to 5.68 Å in good agreement with Yoon's results in this range. On the other hand, for the Mn₃₋ₓCrₓSi alloys it takes constant value of 5.72 Å with respect to the Cr concentration. In analyzing the nuclear contributions to the diffraction data, the site occupation was obtained from measured intensity ratios. The structure factor for (hkl) reflection is given by

\[ F_{hkl} = \begin{cases} b_I - b_{Si} & \text{(for } hkl \text{ all odd)}; \\ b_I + b_{Si} - 2b_{II} & \text{(for } \frac{h+k+l}{2} = \text{odd)}; \\ b_I + b_{Si} + 2b_{II} & \text{(for } \frac{h+k+l}{2} = \text{even)}; \end{cases} \]

where \( b_I \) is the scattering amplitude of the site-I of 8 Mn neighbors, \( b_{II} \) is that of the site-II of 4 Mn and 4 Si neighbors, and \( b_{Si} \) that of the Si site. The results clearly support a model of L2₁ structure, and indicate that Cr prefers the site-I and Fe does the site-II. This tendency of the site preference can be mentioned in the more general words, i.e., "Heavier atoms prefer to occupy the site-II". This is consistent with the site preference observed in the alloying of Fe₂Si with other 3d transition metals³).

The magnetic susceptibility measurements show all samples are antiferromagnetic. The magnetic contribution shows the presence of antiferromagnetic lines for all concentration, and in the range 0<x<0.1 , 0<y<0.1 a incommensurate magnetic structure are observed.
In order to determine the magnetic structure, we use the transversal sinusoidal ordering model which was suggested by Tomiyoshi\(^1\). The magnetic moment of the site-I and the site-II are given as follows

$$\mu_I \mathbf{r}_j^I = \mu_I \sin(\mathbf{q} \cdot \mathbf{r}_j^I) \mathbf{v};$$

$$\mu_{II} \mathbf{r}_j^{II} = \mu_{II} \sin(\mathbf{q} \cdot \mathbf{r}_j^{II} + \theta) \mathbf{v}.$$  

The wave vector $\mathbf{q}$ is $[0.425, 0.425, 0.425]$ for Mn$_3$Si, and for the case of the commensurate structure it is $[0.5, 0.5, 0.5]$. $\theta$ indicates the phase relation between two sites which was determined from observed intensity. Our data showed $\theta = 180^\circ$, except for $y = 1.2$, in which $\theta = 90^\circ$.

Analytic result is as follows. For $0 \leq x \leq 0.2$, and $0 \leq y \leq 0.2$, $\mu_I$ is $2.0 \sim 2.5 \mu_B$, and $\mu_{II}$ is $0.2 \sim 0.4 \mu_B$ with a magnetic axis aligned parallel to (111) plane. For $0.4 \leq y \leq 1.0$, $\mu_I$ is $2.1 \sim 2.8 \mu_B$ and $\mu_{II}$ is $0.1 \sim 0.2 \mu_B$. For the value of $y = 1.2$, a further structural change appeared with a magnetic axis along the (111) direction. The moment for $\mu_{II}$ increases up to $1.4 \mu_B$, in contrast to $\mu_I$ which has little variation of $2.6 \mu_B$.

Existing region of the incommensurate magnetic structure is relatively narrow concentration range of $0 \leq x \leq 0.1$ and $0 \leq y \leq 0.1$. But these values are not so small compared with that of bcc Cr case. Cr becomes paramagnetic at 0 K by 4% doping of V, and changes to the commensurate structure by 0.7% doping of Fe. These results show that the incommensurate spin density wave is stable under some restricted condition, and it is consistent with the fact that there are very small number of magnet show the incommensurate spin density wave.

ACKNOWLEDGMENTS

The authors would like to thank Messrs. K.Nemoto, N.Minakawa and Y.Shimojo for assistance in the neutron diffraction experiments.

REFERENCES

CRYSTAL FIELD STATE AND MAGNETIC ORDERING OF A LOW CARRIER SYSTEM CeP UNDER HIGH PRESSURE AND MAGNETIC FIELD

T. OSAKABE, M. KOHGI, T. SUZUKI, Y. HAGA, #N. MÔRI, #H. TAKAHASHI and †S. IKEDA

Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan
#Institute for Solid State Physics, University of Tokyo, Roppongi, Tokyo 106, Japan
†National Laboratory for High Energy Physics, Tsukuba 305, Japan

CeP is a low carrier system which exhibits a Kondo-lattice-like anomaly in the electrical resistivity. It shows also complicated phase diagrams under high pressure and under high magnetic field. This indicates that the 4f electronic state in this compound is quite sensitive to the atomic distance and magnetic field. In order to study the origin of the anomalous phenomena from the microscopic point of view, we performed neutron scattering experiments under high pressure as well as under magnetic field.

Well-defined crystal field excitations were observed at 0.8 GPa. However the peak position of the crystal field excitation decreases by about 10% by applying the pressure. The decrease of the crystal field splitting under pressure is quite anomalous. It may explain the pressure dependence of the broad maximum observed in the resistivity.

We also measured the magnetic field dependence of the magnetic Bragg scattering. The result indicates that type-I antiferromagnetic structure changes to the structure which includes the ferromagnetic component by applying the magnetic field of 2 T.
INELASTIC NEUTRON SCATTERING MEASUREMENTS ON HYDROGEN-INVOLVED MOLECULAR LIBRATIONS IN SUPERCONDUCTING \( \kappa-(\text{hs-BEDT-TTF})_2\text{Cu(NCS)}_2 \)

N. TOYOTA, T. KAJITANI, T. SHIMAZU, K. SHIBATA, T. SASAKI, M. LANG

Institute for Materials Research, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai, Japan 980

S. IKEDA

Booster Synchrotron Utilization Facility
National Laboratory for High Energy Physics
1-1 Oho, Tsukuba-shi, Ibaraki, Japan 305

ABSTRACT

TOF inelastic neutron scattering measurements using LAM-D spectrometer on a superconducting \((T_c=10\text{K})\) organic salt, \( \kappa-(\text{hs-BEDT-TTF})_2\text{Cu(NCS)}_2 \) are performed to study hydrogen-involved molecular librations. The generalized partial density-of-state (GPDOS) spectrum consists of a broad peak in the low energy regime, 0–25meV, and two rather sharp peaks centered at 32meV and 56meV. The latter peaks, which are also observed in the neutral BEDT-TTF crystal, can be well assigned to hydrogen-involved librations previously calculated and measured in infrared and Raman spectroscopies by Koziol et al. These peak intensity exponentially increases with decreasing temperature down to 18K, followed by a sudden drop at 6K below \( T_c \). Alternatively there appear, at 6K, new low-lying states with three distinct peaks centered at about 2, 4 and 8meV. These energy range is comparable to the superconducting energy gap of 3.5–4.0meV, suggesting that these hydrogen-involved molecular librations might be strongly coupled to superconductivity.

INTRODUCTION

Recently there has been increasing interest in BEDT-TTF-based organic salts, where BEDT-TTF is an abbreviation of bis[ethylenedithio]tetra(thiafulvalene with its chemical formula of CuS$_2$S$_4$. Usually this donor molecule forms a salt with an anion molecule \( X \), \([(\text{BEDT-TTF})_2]^+X^-\), by stoichiometric transfer of an electron per two BEDT-TTF’s onto \( X \). A variety of \((\text{BEDT-TTF})_2X\) salts with different anions or different crystal structures for a given \( X \) has been syn-
thesized in the last decade. One of the most important progress is the discovery of high-\(T_c\) superconductivity around 10K in a salt with \(X=\text{Cu(NCS)}_2\) by Urayama et al.

The crystalline symmetry is monoclinic: the space group \(P2_1\), \(a=1.6242\text{nm}, b=0.8448\text{nm}, c=1.3136\text{nm}, \beta=110.32^\circ, V=1.6901\text{nm}^3, Z=2\). Figure 1 shows the \(\text{BEDT-TTF}\) molecule and the crystal structure in a unit cell projected along the \(b\)-axis. The central fragment \(\text{TTF (CsS)}\) is almost planar, while the outer \(\text{BEDT}\)

![Diagram](image)

\[
\text{H}_2\text{C-S-S-CH}_2 \\
\text{H}_2\text{C-S-S-CH}_2
\]

\(\text{hs-BEDT-TTF}\)

Fig.1 (a) Molecular structure of \(\text{hs-BEDT-TTF}\). (b) Projection of the monoclinic crystal structure of \(\kappa-(\text{hs-BEDT-TTF})_2\text{Cu(NCS)}_2\) along the \(b\)-axis.

(6-member ring, \(\text{CsS\text{H}_4}\)) are out of plane. Although not shown in this figure, \(\text{BEDT-TTF}\)'s are dimerized such that each dimer is almost orthogonally arranged in the \(bc\) plane. This characteristic stacking is called a \(\kappa\)-type, where \(\pi\)-orbital overlappings between sulfurs on neighboring \(\text{BEDT-TTF}\)'s can be highly isotropic in the conducting \(bc\) plane due to both the intradimer face-to-face and the interdimer side-by-side overlappings.

As shown in the figure, the stacking plane is sandwiched by a very thin insulating layer formed by polymeric anions \((\text{SCN-Cu(NCS)})_n\) running along the \(c\)-axis. Hydrogens at the terminal ethylene couple to nitrogen or carbon of the anion, via so-called hydrogen bonding. Anomalous thermal expansion is
observed by four-circle X-ray diffraction measurements that the interlayer spacing takes a maximum around 100K, while the crystal symmetry does not change down to 13K confirmed by neutron and X-ray diffractions.

One of the most interesting characteristics generally in these molecular crystals is the strong lattice contraction with decreasing temperature, suggesting an existence of strong anharmonicity in lattice dynamics. These might coincide with the large compressibility and Gruneisen parameter observed in the present salt.

The electronic states are two-dimensional with very large anisotropy between intra- and inter-planes due to the layer structure as mentioned above. The π-holes on BEDT-TTF form an almost isotropic, three-quarter filled conduction band, the Fermi surface of which has been established by Sasaki et al's Shubnikov-de Haas quantum oscillations. On the other hand, there has been a controversy for the Cooper-pairing symmetry issue in literatures, based on magnetic-field penetration-depth measurements. Recently some measurements which claimed an existence of the anisotropic pairing are called in question, since extrinsic vortex pinnings are not carefully treated there. Detailed magnetization measurements by Lang et al. have reproduced the predictions from BCS and London theories, providing evidence of the conventional s-wave pairing.

A fundamental question remains: What roles do phonons and/or molecular librations play in superconductivity of these charge-transfer molecular crystals? A neutron spectroscopy has contributed to this kind of issue for a superconductor in general. As far as we notice, however, this powerful tool has not been applied for these organic salts. (Only the diffraction measurements are available in Refs. 4 and 11.) Quite recently we have succeeded in time-of-flight inelastic neutron scattering measurements on κ-(TMTSF)$_2$Cu(NCS)$_2$.

**EXPERIMENTAL**

Single crystals are obtained by a standard electrooxidation method using all the starting materials purified by recrystallization. Usually 2–4 months are needed for completing the crystal growth with the transport current of about 1µA. The crystal is a hexagonal plate with well-grown habit planes. The typical size is about 2x1(bc-plane)x0.05(interlayer)mm$^3$. For the present neutron experiments, we have used the aggregate of these pieces of single crystals of the total weight, about 200mg, corresponding to 100mm$^3$ in volume. These are wrapped by an aluminum foil, and then inserted into an aluminum hollow cylinder.

The spectrometer LAM-D (Lattice-Crystal Analyzer Mirror Spectrometer) of the Booster Synchrotron Utilization Facility at KEK is used; the energy-transfer range of 0–200meV, the resolution of 0.4meV, scattering angles of 35° and 85° with two He$^3$ detectors each for scattered neutrons with 0.422nm wave-length (4.59 meV) monochromated by pyrolytic graphite. The data obtained by high-angle detectors covering the wide momentum-transfer range are used for analysis. Measurements are made at temperatures from 6K to 123K, with and without the sample to subtract the background signals. The neutral BEDT-TTF crystal (645mg in total), which is an insulator of translucent
orange color, is also measured at 6K as a reference material for comparison with the salt.

RESULTS AND DISCUSSIONS

1. Librational Mode Assignment

Since the present salt contains significant amount of hydrogens as shown in Fig.1, inelastically scattered neutrons are expected to be predominantly incoherent from hydrogens, because of the overwhelmingly large incoherent-scattering-crosssection of hydrogen \((79.91(4) \times 10^{-28} \text{cm}^2)\) compared to those of other elements involved in this crystal such as carbon \((0.000(4))\), sulfur \((0.007(5))\), copper \((0.52(4))\), and nitrogen \((0.49(10))\). Therefore the present measurements could have little chance to detect coherent lattice-vibrations, but exclusively provide information of molecular \((\text{H}_2\text{-BEDT-TTF})\) librations associated by hydrogens.

![Diagram showing GPDOS spectra for neutral and salt crystals at 6K.](image)

Fig.2 GPDOS spectra for neutral and salt crystals at 6K.

Figure 2 shows the generalized partial density-of-states (GPDOS) spectra at 6K as a function of the energy transfer up to 60 meV for both neutral BEDT-TTF and salt \((\text{BEDT-TTF})_2\text{Cu(NCS)}_2\). (In the high-energy regime above 60 meV, monotonous background-like spectra of weak intensity are observed.)
In the neutral–salt spectrum are seen several groups of peaks. Kozlov et al.\textsuperscript{13} have calculated frequencies of about 60 molecular–librational modes for a neutral BEDT-TTF, which are in well agreement with their observations by infrared and Raman spectrosopies for the neutral crystal. Their results below 60meV are shown in Fig.2 by solid and dotted arrows, respectively for observations and calculations. As shown in this figure, the present neutron data are found to fairly agree with these: totally symmetric modes $\nu_{10,11,12}(a_6)$ and other non-symmetric modes as $\nu_{SS}(b_{3g})$, $\nu_{SS}(b_{2g})$, $\nu_{SS}(b_{1g})$, $\nu_{SS}(b_{2u})$, $\nu_{SS}(b_{3g})$, and $\nu_{3g}(b_{2g})$. Low lying modes of $\nu_{72}(b_{3g})$ and $\nu_{54}$ could be assigned to the peak around 12–13meV and a hump around 7meV, respectively. It is noted that all these modes associate hydrogen librations and the isotope-shift of frequency by deuteration (d$\alpha$-BEDT-TTF) is consistently observed\textsuperscript{10} with calculations. We conclude here that (1) present measurements on the neutral crystal reproduce previous results from these optical spectroscopy and calculations, and (2) scattered neutrons are exclusively incoherent from hydrogens as expected above.

In Fig.2, one can see the very similarity of the spectrum of the salt in the high-energy regime (say, above 25meV) with that of the neutral crystal, while remarkable dissimilarity in the low-energy regime below 25meV. Since the data for the salt have poor statistics compared to those for the neutral crystal, the mode assignment for the salt is not so clear as for the neutral crystal. The broad peaks centered around 32meV and 56meV, however, can be reasonably ascribed to resultant from corresponding modes for the neutral crystal. A hump-like GPDS observed in the low-energy regime around 15meV might be assigned to $\nu_{54}$ – $\nu_{72}$. In contrast to these high-energy broad peaks in the salt, there are found three distinct peaks below 10meV.

2. Anomalous Spectrum Of The Salt

Figure 3(a) shows how GPDS of the salt changes with temperature. It can be clearly seen that the spectrum shape at high temperatures from 123K down to 18K is similar, associated with peak intensities systematically enhanced with decreasing temperature. The broad peak (0–25meV) and two distinct peaks (centered at 32meV and 56meV) increase with decreasing temperature down to 18K. At 6K, surprisingly, the high energy peaks suddenly lose their intensity, and low-lying three peaks below 10meV appear as already mentioned.

Figure 3(b) shows the temperature dependence of the integrated GPDS for the high energy two peaks at 32meV and 56meV shown by closed and open circles. Both data above 18K can be tentatively fit to $\exp(\varepsilon/k_BT)$ ($\varepsilon$ is a constant) as shown by solid lines. This enhancement disappears at 6K. These anomalous temperature dependence might be attributed to some anomaly in a Debye–Waller factor. Detailed analysis is now under way.

Figure 4 compares GPDS at 18K to that at 6K in the low-energy regime up to 25meV to demonstrate more clearly the difference. It is noted within a statistical error that any difference in the spectrum above 10meV is not found, but something new states appear at 6K with three distinct peaks centered around 2meV, 4meV and 8meV. It is noted here that the energy regime for these new peaks is close to the superconducting energy gap of 3.5-4.0meV estimated from the discontinuous change in the specific heat.\textsuperscript{14}
Fig. 3 (a) Temperature dependence of GPDOS, (b) Integrated intensity of peaks at 32 meV and 56 meV shown by closed and open circles, respectively.

Fig. 4 Comparison of GPDOS at between 6K and 18K.
Finally, above-mentioned anomalies in GPDOS, i.e., the quenching of the growing intensity of high energy peaks and the associated appearance of low-lying new states, might be correlated with the superconducting state, suggesting that hydrogen-involved librational modes could be strongly coupled to superconductivity.

ACKNOWLEDGEMENTS

The authors express sincere thanks Mr. D. Sugimoto and Mr. K. Iwasa for their great help in experiments at KEK, and Prof. N. Watanabe for encouragement.

REFERENCES

[110]TA₁ PHONON DISPERSION RELATIONS OF BCC, B2 AND HEUSLER PHASES IN AuCuZn₂ ALLOY

A. NAGASAWA, R. YAMAUCHI, †T. MAKITA, ‡Y. MORII and ‡S. FUNAHASHI

Department of Physics, Nara Women's University, Nara 630, Japan
†Office of SR Facility. Project, JAERI, Tokai 319-11, Japan
‡Department of Physics, JAERI, Tokai 319-11, Japan

ABSTRACT

The present study by neutron inelastic scattering experiments reveals that characteristics of the [110]TA₁ phonon dispersion relation in the Heusler phase region are never transmitted to either the B2 phase or the bcc phase. The lattice instability towards the 18R martensite begins to occur after the Heusler ordering is completed at about 670K. Anomalous elastic peak appearing near 2/3q_{max} is also studied in a wide range of temperature: we make clear that the peak is due to a certain kind of regular arrangement of vacancies in the B2 phase, as is the case of the ω-like peak in this alloy.

INTRODUCTION

The high temperature bcc phase of AuCuZn₂ alloy undergoes successively three kinds of phase transformations during cooling. In the case of Au-30Cu-47Zn (at %) alloy, for example, the ordering reaction to the B2 phase (CsCl type structure) occurs at about 880K, and subsequently the B2 phase transforms to the L2₁ phase (Heusler type structure) at about 670K. By further cooling, the Heusler phase undergoes martensitic transformation to the 18R structure: the transformation temperature Ms is about 260K for slowly cooled specimen while about 270K for quenched one. Among these phases, the Heusler phase has been extensively studied so far and we have found several kinds of anomalies such as lattice softening, low-energy phonons and diffraction anomaly. It is very meaningful to examine whether such anomalies are associated with the lattice instability as a precursor of the martensitic transformation in the Heusler phase or not. From this point of view, we have studied the anomalies and obtained some remarkable results.

We examined, for example, the origin of the 2/3 q_{max} dip appearing on the [110]TA₁ phonon dispersion relation of many premartensitic B₁ phases.
by the interplaner force constant analysis\textsuperscript{5,7} . The obtained results prove that the premartensitic materials are classified into three groups according to combination of $\Phi_2$ and $\Phi_3$: $\Phi_n$ means the effective interplaner force constant between the $n$-th neighbour (110) atomic planes. If we know the constants $\Phi_2$ and $\Phi_3$ of any premartensitic state, we can predict the structure of its martensite to be formed. Therefore it is very interesting problem to extend the interplaner force constant analysis to the other materials than the $\beta$ phase alloys undergoing the martensitic transformation.

Recently, we have examined\textsuperscript{10} also the $\omega$-type diffraction anomaly appearing in the quenched Heusler phase, and revealed that such an anomaly is originated from a certain kind of regular arrangement of vacancies in the incompletely ordered B2 phase, the vacancies which act as a go-between for the ordering reaction to the Heusler type lattice: they are frozen into the Heusler phase formed by quenching. This result means that detailed investigation of the B2 and bcc phases is very important to understand the nature of the premartensitic state in AuCuZn$_2$. From this viewpoint, we have carried out lattice dynamical studies of AuCuZn$_2$ in a wide range of temperature above room temperature. The present paper gives briefly a temperature dependent behaviour of the [110]TA$_1$ phonon dispersion relations of the Heusler, B2 and bcc phases. The result of the interplaner force constant analysis is also presented. In addition, in order to understand the relation between the 2/3 $q_{\text{max}}$ dip on the [110]TA$_1$ phonon branch and diffraction anomalies, we report the result of the study on the temperature dependence of elastic peak appearing at 2/3$q_{\text{max}}$.

EXPERIMENTAL PROCEDURE

In the present study, we examined the single crystal of Au-30Cu-47Zn alloy used in the previous study on the $\omega$-like anomaly\textsuperscript{5} . The transformation temperatures were determined by electric resistivity measurements and DSC method. The Heusler and B2 phases are stable between 260 and 670K and between 670 and 880K, respectively. The bcc phase exists above 880K. Elastic and inelastic neutron scattering experiments were performed on the triple axis spectrometer TAS-1 or TAS-2, with incident neutron energy of 14.79 meV ($\lambda = 0.2352$ nm), installed at JRR-3M in Tokai. Tuned pyrolytic graphite filters were used to eliminate wavelength contamination. Experiments above room temperature were carried out in N$_2$ atomosphere in an electric furnace equipped on the spectrometer.

RESULTS AND DISCUSSION

The [110]TA$_1$ phonon dispersion relation has been so far measured only
in the region of the Heusler phase\textsuperscript{2,4,5} and it has been well proved that the phonon branch in question is low-lying and exhibits throughout slight softening with decreasing temperature. It is also known that a dip appears at $2/3q_{max}$ and grows by cooling. In the B2 and bcc phases, however, the $[110]TA_1$ branch shows quite different behaviours from that of the Heusler phase as observed in the present study.

![Graph](image)

**Fig. 1.** The $[110]TA_1$ phonon dispersion relations of the Heusler, B2 and bcc lattices. The solid lines serve merely as a guide to the eye.

Figure 1 depicts en bloc the phonon branches in question of three kinds of phases. The dispersion curves of the B2 and bcc phases are smooth; the dip is not noticeable as is the case of the Heusler phase. Characteristics of temperature dependent phenomena of phonon energies can be seen in Fig.2, where phonon energies at $q = 0.2q_{max}$ and $0.6q_{max}$ are shown as a function of temperature. It is clear that the $[110]TA_1$ branches of both B2 and bcc phases behave normally to the temperature change, while corresponding phonon mode of the Heusler phase exhibits a slight softening by cooling. Consequently these results indicate evidently that the dynamical instability towards the 18R martensite begins to occur just after the Heusler ordering is completed at about 670K.

The interplanar force constant analysis has been also performed for the $[110]TA_1$ dispersion relations of the Heusler, B2 and bcc phases. Table 1 summarizes the obtained results: $\Phi_2$ and $\Phi_3$ are the ratio to $\Phi_1$. 

---

488
As seen in Table 1, the force constants $\Phi_2$ and $\Phi_3$ of the Heusler phase are respectively negative and positive, and their absolute values increase with decreasing temperature. As already reported\textsuperscript{5-7)}, this situation indicates that the lattice instability towards the 18R martensite is gradually enhanced with decreasing temperature. In the B2 phase region, however, both $\Phi_2$ and $\Phi_3$ are positive but considerably very small. This means that the first nearest neighbour coupling force rules dominantly the B2 lattice like a harmonic lattice. In the bcc phase region, on the other hand, $\Phi_2$ becomes positive while $\Phi_3$ is negative. Since the bcc phase melts upon heating, characteristics of these interplaner force constants would suggest a schema of instability towards the melting. Anyway it is certain that dynamical properties of the Heusler phase are transmitted to neither the B2 nor the bcc phase. This is quite compatible with phonon behaviours.
mentioned above.

It is well known that the elastic scattering appears near the 2/3 \( q_{\text{max}} \) position on the \langle 110 \rangle lines of the reciprocal lattice. Since the wave vector 2/3\( q_{\text{max}} \) corresponds to that of a lattice wave for the Heusler to 18R modulation, the anomalous peak would be considered to be a certain kind of precursor behaviour to form the 18R martensite. Such an anomaly, however, has been found even in the \( \beta_1 \) phase of Cu-Al-Ni alloy\(^\text{9}\), although the alloy transforms to the 2H martensite by cooling: the 2/3[110] \( q_{\text{max}} \) peak appears regardless of the martensite structure to be formed. Consequently, it is very significant to investigate the nature of the 2/3[110]\( q_{\text{max}} \) peak, especially its temperature dependence in detail.

![Graph showing temperature dependence of neutron scattering intensity](image)

**Fig. 3.** Temperature dependence of neutron scattering intensity of the 2/3[110] \( q_{\text{max}} \) peak.

Under these circumstances, we have measured elastic scattering intensity of the 2/3[110] \( q_{\text{max}} \) peak, appearing in the specimen quenched from 873K, in a wide range of temperature. Figure 3 depicts some of the obtained results. We can see that the 2/3[110] \( q_{\text{max}} \) peak intensity disappears with increasing temperature in the Heusler phase region. Such a phenomenon corresponds well to that of the temperature dependence of the 2/3\( q_{\text{max}} \) dip of the [110]\( \beta_1 \) phonon branch. When heated to the B2 phase region, however, the peak appears suddenly with strong intensity at the position corresponding to 2/3[110] \( q_{\text{max}} \), of the Heusler phase, while the 2/3\( q_{\text{max}} \) dip is not restored. Consequently, it is clear that the origin of such an anomalous peak is really different from that of the 2/3 \( q_{\text{max}} \) phonon anomaly.
We must notice that the temperature dependent feature of the 2/3[110] \( q_{m.a} \) peak resemble very much that of the \( \omega \)-like peak observed in the quenched \( \beta_1 \) phase\(^8\). Thus, it is reasonable to suppose that, just as is the case of the \( \omega \)-like peak, the the 2/3[110] \( q_{m.a} \) is due to a certain kind of regular arrangement of vacancies existing in the B2 phase. In order to prove our view, we need to establish a model for regular arrangement of vacancies in the B2 lattice.

Acknowledgment

The present study is supported in part by the Grant-in-Aid for Scientific Research under Contract No. 04452043 and 04302053 from the Ministry of Education, Science and Culture of Japan. We would especially like to thank N. Minakawa and Y. Shimojo, Department of Physics, JAERI, for their support for our neutron scattering experiments.

REFERENCES

HIGH PRESSURE NEUTRON DIFFRACTION STUDIES OF THE MAGNETIC STRUCTURES OF Tb, Ho AND Er

1Shinji KAWANO, 2Norio ACHIWA, 3Akifumi ONODERA, 4Yutaka NAKAI and 5Bente LEBECH

1Research Reactor Institute, Kyoto University, Kumatori, Osaka 590-04, Japan
2Faculty of Science, Kyushu University, Fukuoka 812, Japan
3Faculty of Engineering Science, Osaka University, Toyonaka 560, Japan
4Shizuoka Institute of Science and Technology, Fukuroi, Shizuoka 437, Japan
5Department of Solid State Physics, Risø National Laboratory, DK-4000, Roskilde, Denmark

ABSTRACT

Pressure effects of the magnetic structures of Tb, Ho and Er have been studied by neutron diffraction using a newly-developed clamp type pressure cell. For Tb the pressure dependence of the turn angle in a helical phase shows an enhancement of its value, particularly in low temperatures with increasing pressure but no lock-in feature. Linear coefficients of the magnetic transition temperatures to pressure are obtained. For Ho the turn angle is increased by pressure and shows an almost linear temperature dependence at high temperatures and lock-in features at low temperatures. For Er the high pressure results reveal that the transition to a conical structure at low temperatures is suppressed and that a cycloidal structure with a modulation vector $Q=2\pi(2\pi/c)$ persists down to 4.5 K, similar to a three up four down structure in Tm.

INTRODUCTION

As is generally accepted, helical or oscillatory magnetic orderings in rare earth metals and alloys are attributed to the results of a compromise between competing magnetic interactions such as indirect RKKY interaction, one-ion and two-ion anisotropy effects and magnetoelastic effects [1]. The dependence of the magnetic structures on interatomic distance should provide information on these competing interactions and lead us to a deeper understanding of the transitions between the observed
various spin configurations. Therefore, high pressure studies have been extensively performed on their magnetic properties [2-10]. Most of them in the past decades are measurements of electrical resistance or initial permeability, so that a detailed magnetic structure has remained unclear so far [2-6]. Though Umebayashi et al. [7] have made neutron diffraction studies of the effects of pressure on Tb and Ho, an experimental range of pressure and temperature was slightly limited to 0-0.6 GPa and room temperature-80K, respectively, because of using helium gas-pressure facilities. Recently we have developed a McWhan-type [11] high pressure cell for neutron scattering [12] and have used it successfully to examine pressure effects on the magnetic structures of Ho [8], Tb [9] and Er [10] over a wide pressure and temperature range (from 0 to 2.5 GPa and from 10 to 300K) by neutron diffraction. In the present report, we summarize the high pressure neutron diffraction studies of the magnetic structures of Tb, Ho and Er above mentioned.

EXPERIMENTAL

Single crystals prepared with a usual strain-annal method was placed in the high pressure cell, available up to hydrostatic ~3GPa together with a single crystal of NaCl as a pressure marker. The pressure was monitored by a measurement of the lattice compression of NaCl. The pressure cell was mounted on a cold tip of a close-cycle gas-He refrigerator or of a variable temperature He°C cryostat. The neutron diffraction experiments for Tb, Ho, and for Er were carried out at Kyoto University Reactor using the TAS spectrometer (KUR-TAS) with incident neutrons of 1.007A and at Riso National Laboratory, Denmark using the TAS6 spectrometer with incident neutrons of 2.453A, respectively, in the two-axis mode. The data were collected for the (HHL) type reflections and the diffracted intensities were normalized to constant monitor counts by means of a neutron beam monitor.

RESULTS AND DISCUSSION

Tb

As shown in Fig. 1, there exist three magnetic transition temperatures $T_N$, $T_C$ and $T_F$ under pressure with temperature. The helical phase appears within a narrow temperature interval from $T_N$ to $T_F$, while between $T_C$ and $T_F$ both of helical and planar ferromagnetic phases coexist. Pressure causes a reduction of these three transition temperatures and appears slightly to expand the temperature interval for the helical phase. Table 1 summarizes the coefficients of linear shift for the transition temperatures with pressure. The obtained coefficients are in fair agreement with the results up to 0.276 GPa by Umebayashi et al. [7].

Figure 2 gives the turn angle $\omega$ of a helical structure for Tb under pressure. The curve at ambient pressure generally
agrees with the results [13] reported previously, including the s-figure temperature dependence. With increasing pressure this s-figure behavior appears slightly to collapse and an increase in $\omega$ is remarkable at lower temperatures, where a planar ferromagnetic component develops rapidly with a simultaneous reduction of the helical component. There is no lock-in feature in the temperature dependence of $\omega$ within these pressures. It is likely that the development of the ferromagnetic component is responsible for the s-figure behavior and no lock-in feature. They may be correlated each other, as suggested by Kaino and Kasuya [14].

![Graph showing neutron count vs. temperature for Tb under high pressure](image1)

**Fig. 1.** Thermal variation of the peak intensities of (002) and the (002) reflections.

![Graph showing turn angle vs. temperature for Tb under high pressure](image2)

**Fig. 2.** Temperature dependence of helical turn angles on warming process.

<table>
<thead>
<tr>
<th>Magnetic properties of Tb under high pressure.</th>
<th>ambient</th>
<th>1.03 GPa</th>
<th>1.93 GPa</th>
<th>linear coefficient (/GPa) present</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_N$ (K)</td>
<td>231</td>
<td>228</td>
<td>225</td>
<td>215 d$T_N$/dp=-8.2 K</td>
</tr>
<tr>
<td>$\omega_1$ (deg)</td>
<td>20.6</td>
<td>20.5</td>
<td>23.4</td>
<td>24.2 $\omega_1$ d$\omega_1$/dp=0.1</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>225</td>
<td>225</td>
<td>217</td>
<td>200 d$T_C$/dp=-12.8 K</td>
</tr>
<tr>
<td>$T_F$ (K)</td>
<td>218</td>
<td>217</td>
<td>206</td>
<td>192 d$T_F$/dp=-13.4 K</td>
</tr>
<tr>
<td>$\omega_F$ (deg)</td>
<td>18.0</td>
<td>18.0</td>
<td>23.3</td>
<td>29.0 $\omega_F$ d$\omega_F$/dp=0.3</td>
</tr>
</tbody>
</table>

a) $\omega$ at $T_N$. b) $\omega$ at $T_F$. c) Extrapolated to $T_F$.

The temperature dependence of the helical turn angle $\omega$ is shown at various pressures in Fig. 3. The pressure produces a rather large enhancement of $\omega$ and a lock-in feature below
~30K, whereas it gives an almost linear temperature dependence above ~30K. According to a free electron model the helical turn angle depends on energy gaps \( \omega = M(V/E_F) \) at magnetic superzone boundaries and a spin disorder scattering parameter \( \gamma = (9\pi/8)(S^2-M^2)/(V/E_F)^2 \). Here \( S \) and \( M \) are the spin magnetic moment at 0K and TK, respectively, \( V \) the exchange potential and \( E_F \) the Fermi energy of conduction electrons. Figure 4 shows equal turn angle contours on the \((\omega, \gamma)\) plane given by Miwa [16], in which the obtained turn angles are plotted along \( t = T/T_N \) lines. If \( t = T/T_N \) is constant, then \( M \) is constant, so that \( \omega \) should be on the straight line through the origin. If pressure is constant, then \( V \) is constant, so that \( \omega \) should be expressed by a linear line. The lines for different pressures have different inclinations but converge at the \((0,4)\) point. At 2.1 GPa the line crosses the abscissa at \((3,0)\) instead of \((4,0)\) at ambient pressure. This means that the ambient squared exchange potential is reduced by 25% at 2.1 GPa.

Below 20K \( \omega \) shows a lock-in feature. The lock-in turn angles are 31°, 36° (commensurate 2/10), 40° (commensurate 2/9) and 41° at ambient pressure, 0.7GPa, 1.6GPa and 2.1GPa, respectively. Recent studies of Ho by magnetic scattering with synchrotron radiation have shown the presence of spin slips for the lock-in phase with a commensurate modulation in the helical structure [17]. The present 31° and 41° structures would be produced from a proper combination between commensurate 30° and 32.72° (2/11) structures and between commensurate 40° and 45° structures, respectively. An actual structure should appear as a mixture of such various slip structures in order to reduce a lattice distortion associated with introduced spin slips.

Fig. 3. Temperature dependence of the helical turn angle. The dashed line (ambient) is from Koehler et al.[15] and 0.6GPa(\( \Delta \)) from Umebayashi et al.[7].

Fig. 4. Contours of equal turn angles plotted in the \((M^2, S^2-M^2)\) plane [16].

Turn angles are plotted along \( t = T/T_N \) line, where \((S^2-M^2)/M^2\)-constant but \((V/E_F)\) is modified with the pressure in the same figure.

---

495
Er

Figures 5 and 6 show neutron diffraction patterns at 4.5K and hydrostatic 1.15 GPa, scanned along the (0,0,L) and (1,1,L) direction, respectively. There is no higher harmonics component along the (0,0,L) direction but higher harmonics up to the seventh one along the (1,1,L) direction, because the observed modulation vector $Q=2/7(2\pi/c)$ means that a ferromagnetic component corresponds to the seventh harmonics. From those patterns it is concluded that the transition from a cycloidal to conical structure at ambient pressure is entirely suppressed by pressure and the cycloidal structure persists down to low temperature 4.5K.

Fig. 5. Diffraction patterns for Er at 1.15GPa by scanning along the [00L] direction. Figures (a) and (b) show the patterns at 95K, well above $T_N$ and at 4.5K, respectively. Figure (c) is the difference between (a) and (b), i.e. only the magnetic scattering. The peaks marked A~J are reflections from the Al$_2$O$_3$ pressure-supporting device.

Fig. 6. Diffraction patterns for Er at 1.15GPa by scanning along the [11L] direction. Figures (a) and (b) show the patterns at 95K, well above $T_N$ and at 4.5K, respectively. Figure (c) is the difference between (a) and (b), i.e. only the magnetic scattering. The peaks marked F~J are reflections from the Al$_2$O$_3$ pressure-supporting device.

The obtained intensities have been analyzed according to the following cycloidal model with Er atoms at $r_n$ in the $n$th
hexagonal basal plane:

\[ \mu_x(n) = \mu_0 \cos(\mathbf{r}_n \cdot q + \alpha_x) \]
\[ \mu_y(n) = \mu_0 \cos(\mathbf{r}_n \cdot q + \alpha_y) \]
\[ \mu_z(n) = A_1 \cos(\mathbf{r}_n \cdot q + \gamma_1) + A_3 \cos(3\mathbf{r}_n \cdot q + \gamma_3) + A_5 \cos(5\mathbf{r}_n \cdot q + \gamma_5) \]

where \( x, y \) and \( z \) refer to moment components in the \( a-, b- \) and \( c- \) direction of the real space lattice. Each moment component can be determined from the magnetic intensities. Though neutron diffraction cannot usually yield the phase angles for each harmonics component, in the present case the modulation is commensurate with \( q = 2/7(2\pi/c) \), so that they can be evaluated by a trial and error method with the following conditions: (1) within experimental errors the total moment on any Er should not exceed the free ion value of \( 9\mu_B \) per Er atom. (2) the moment of all atom should be as large as and of as equal length as possible, and (3) \( \mu_0 \) which causes the plane of the cycloidal spin configuration to wobble, is assumed to be negligible. The results are summarized in Tables 2 and 3, together with those obtained from the same analysis of ambient data by Habenschuss et al. [17].

**Table 2.** The magnetic structures of Er at 1.15 GPa and at ambient pressure. *For the helical structure \( \mu_\perp = (1/\sqrt{2}) \mu_x0 \)

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Ambient, 4.5k Cycle</th>
<th>Cycloid, 4.5k Present Work</th>
<th>Ambient, 22K Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15 GPa</td>
<td>Habenschuss et al. [18]</td>
<td>Habenschuss et al. [18]</td>
<td></td>
</tr>
<tr>
<td>( \mu_x0 = 4.41(0.34) )</td>
<td>( \mu_y0 = 4.44 )</td>
<td>( \mu_x0 = 5.4 )</td>
<td></td>
</tr>
<tr>
<td>( \mu_y0 \sim 0 )</td>
<td>( A_1 = 10.16(0.64) )</td>
<td>( \mu_\perp \neq 0, n = 3, 5 )</td>
<td></td>
</tr>
<tr>
<td>( A_3 = 3.33(0.06) )</td>
<td>( A_5 = 2.67(0.07) )</td>
<td>( A_1 = 10.5 )</td>
<td></td>
</tr>
<tr>
<td>( A_1 = 1.83(0.24) )</td>
<td>( A_3 = 2.5 )</td>
<td>( A_5 = 1.2 )</td>
<td></td>
</tr>
<tr>
<td>( \mu_\perp = 3.12(0.24) * )</td>
<td>( A_7 = 0.8 )</td>
<td>( \mu_\perp = 3.8 * )</td>
<td></td>
</tr>
</tbody>
</table>

| \( q = 2/7(2\pi/c) \) | \( Q = 5/21(2\pi/c) \) | \( Q = 2/8(2\pi/c) \) |

**Table 3.** The phase angles determined by the method described in the text. The notation is the same as that used in Eq. (1).

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Ambient, 22K Cycle, Fig. 7a</th>
<th>Cycloid, Fig. 7b Present Work</th>
<th>Ambient, 22K Cycle, Fig. 7c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.15 GPa</td>
<td>Habenschuss et al. [18]</td>
<td>Habenschuss et al. [18]</td>
<td></td>
</tr>
<tr>
<td>( \alpha_x = \pi/2 )</td>
<td>( \alpha_x = -\pi/4 )</td>
<td>( \alpha_x = \pi/8 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma_1 = 0 )</td>
<td>( \gamma_1 = \pi/4 )</td>
<td>( \gamma_x = -3\pi/8 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma_3 = \pi )</td>
<td>( \gamma_3 = -\pi/4 )</td>
<td>( \gamma_3 = -\pi/8 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma_5 = 0 )</td>
<td>( \gamma_5 = 5\pi/4 )</td>
<td>( \gamma_5 = \pi/8 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma_7 = \pi )</td>
<td>( \gamma_7 = -5\pi/4 )</td>
<td>( \gamma_7 = -5\pi/8 )</td>
<td></td>
</tr>
<tr>
<td>( q = 2/7(2\pi/c) )</td>
<td>( Q = 2/8(2\pi/c) )</td>
<td>( Q = 2/8(2\pi/c) )</td>
<td></td>
</tr>
</tbody>
</table>
According to the obtained phase angles and the moment components in tables 2 and 3, Fig. 7 depicts the spin configuration of the cycloidal structures in Er. In the present high pressure case a cycloidal modulation is commensurate with \( Q = 2/7(2\pi/c) \), so that a ferromagnetic component can be directly evaluated from the seventh harmonics satellites. This fact means that the phase of the seventh harmonics is no longer a free parameter, it must be either 0 or \( \pi \). Although another set of the phase angles, \( \pi/2, 0, \pi, 0 \) and \( 2\pi/3 \) fulfills the above three conditions better than the values in the table 3, the corresponding structure is not the correct commensurate structure because the ferromagnetic component will be too small \( (A_7 \cos(2\pi/3)) \) instead of \( A_7 \).

![Fig. 7. Spin configuration for a cycloidal structure of Er at 4.5K and at 1.15GPa (a). The moments have been projected onto the xz-plane and displaced to a common origin. The numbers \( n = 0 \) to 7 refer to the \( n \)th layers of atoms. (b) and (c): possible cycloids at 22K and at ambient pressure from data given by Habenschuss et al. [18]. See tables 2 and 3.](image)

The cycloidal structure of Er at 1.15 GPa and at 4.5K shown in Fig. 7a has a net ferromagnetic moment of \(-1.8 \pm 0.3 \mu_B\) along the c-axis. A maximum deviation of a spin from the c-axis is about 26°. The structure is almost a three-up-four-down structure similar to the one observed in Tm metal by Koehler et al. [19]. In Tm, the spins in plane perpendicular to the c-axis are ferromagnetically aligned parallel to the c-axis in a three-up-four-down sequence with modulation vector of \( Q = 2/7 \) along the c-axis.

Figures 7b and 7c show two possible spin configurations determined in the same way as above mentioned from the data of Habenschuss et al. [18] at ambient pressure and at 22K. From neutron diffraction alone it is impossible to decide which of these two structures is correct. The structure shown in Fig. 7b is highly anisotropic; the second and sixth spins are in the basal plane while the remaining spins are predominantly along the c-axis. Due to strong magnetoelastic effects in Er [17] this configuration will lead to a lattice distortion with a periodicity of \( Q = 4/8 \). In contrast, the structure shown in Fig. 7c is relatively isotropic with all spins predominantly along the c-axis and will lead to a relatively small lattice distortion. Therefore, precise X-ray experiments may allow us to distinguish between these two structures.
ACKNOWLEDGEMENT

The authors gratefully acknowledge stimulating discussions with Dr. J. Jensen and Dr. A.R. Mackintosh.

The high pressure cell used for the present work has been developed under the auspices of the US-Japan Cooperative Program in Neutron Scattering supported by the US Department of Energy and the Ministry of Education, Science and Culture, Japan.

Part of this work was performed under the visiting research program of the Research Reactor Institute, Kyoto University.

REFERENCES

NEUTRON QUASI-ELASTIC SCATTERING STUDY OF MAGNETIC FLUCTUATIONS IN Yb MONOPNICTIDES

Kenji OHYAMA, Masahumi KOHGI, Toshiya OTOMO, Toyotaka OSAKABE, Akira OYAMADA and Takashi SUZUKI

Department of Physics
Tohoku University
Aramaki Aoba Sendai, 980 Japan

Institute for Materials Research
Tohoku University
Katahira Aoba Sendai, 980 Japan

ABSTRACT

We present results of an investigation of spin dynamics of the semimetallic Kondo compounds YbX (X=N, P, As) by neutron quasi-elastic scattering (QES) experiments. The spin dynamics in YbX is found to be essentially the same independent of X. The crossover of QES spectra from Gaussian-like form to Lorentzian-like one occurs around 150K with the increase of temperature. This crossover behavior indicates that the spin fluctuations at low temperature region are governed by the RKKY type interatomic exchange interactions, but the single site relaxation process becomes important at higher temperatures. It is concluded that the Kondo effect suppresses strongly the magnetic long range ordering in YbX.

INTRODUCTION

Ytterbium monopnictide, YbX(X=N, P, As), which crystallizes in the NaCl structure, is a semimetallic compound with very low carrier density (a few percent per formula). The crystal field (CF) level scheme was reported to be that $\Gamma_6$ is ground state with $\Gamma_8$ and $\Gamma_7$ as the first and second excited states, respectively\(^3\). At a low temperature around 0.5K, YbX undergoes antiferromagnetic long range ordering\(^1\), where the Néel temperatures of YbN, YbP and YbAs are 0.735K, 0.41K and 0.49K, respectively\(^2\). However, the entropy of YbP at $T_N$ is only 20% of Rln2 which is the expected value of the ground state doublet, $\Gamma_6$\(^2\). The saturated magnetic moment in the ordered state are considerably smaller than the expected value of $\Gamma_6$ (1.33$\mu_B$). A Kondo-like enhanced magnetic specific heat is also seen around 5K\(^1\). The electronic specific heat coefficient $\gamma$ of YbAs was estimated to be about 250 mJ K$^{-2}$mole$^{-1}$\(^4\). These are the characteristic features of a Kondo system with magnetic long range ordering. In order to understand the origin of the anomalies from the microscopic point of view, we have studied the magnetic excitation and spin dynamics in YbX by means of neutron inelastic and quasi-elastic scattering (QES) experiments. Some results of our previous work were reported elsewhere\(^5\)\(^6\)\(^7\). In this paper, we report the results of QES experiments in YbX.
EXPERIMENTAL

Polycrystalline samples of YbN were prepared by reacting flakes of metal Yb in an open tungsten crucible at a nitrogen pressure of 1300 atm at 1500°C for 6 hours. Polycrystalline samples of YbP, YbAs were prepared by synthesizing initial material of the required composition in a closed quartz tube at 600°C for two weeks. X-ray diffraction records at room temperature showed only the expected NaCl reflections for all samples.

We performed neutron QES experiments on powder samples of YbN, YbP and YbAs using the crystal analyzer type neutron spectrometer, LAM-D, at the spallation neutron source, KENS, in National Laboratory for High Energy Physics, KEK. LAM-D uses a fixed final neutron energy of about 4.5meV. This condition in LAM-D facilitates high resolution experiments in lower energy transfer region. We also measured Q-dependence of QES spectra in YbX using the triple axis spectrometer, TOPAN, at the JRR-3M in Japan Atomic Energy Research Institution, JAERI. The polycrystalline samples of about 20g(YbN), 60g(YbP), 50g(YbAs) were used in the neutron scattering experiments.

(a)  
(b)

Fig.1 QES spectra in YbN using LAM-D with $E_F=4.5$ meV at 14 K and at room temperature. The solid lines indicate the Gaussian (a) and Lorentzian (b) spectra convoluted with the instrumental resolution. The chain lines and dotted lines show the quasi-elastic and incoherent elastic parts of the spectra, respectively.
RESULTS AND DISCUSSION

Figure 1 shows QES spectra of YbN measured with LAM-D at a scattering angle of 35° at 14K, 26K, 50K, 150K and room temperature. Figures 1(a) and (b) show the same observed spectra and results of different methods of analysis, as described below. The observed spectra (open circles) were corrected for the background, absorption and wavelength dependence of incident neutron flux. The chain lines in the figures show the results of the least squares fit of the QES spectra to either a Gaussian (fig.1(a)) or a Lorentzian (fig.1(b)) as the spectral function. In the fitting procedure, the convolution of the instrumental resolution was taken into account. The dotted lines in the figures correspond to the incoherent elastic scattering parts of the spectra and indicate the energy resolution as well. Here, we do not discuss the temperature dependence of the intensity, because the experimental conditions for these spectra are not identical. As seen in the figures, the QES spectra at lower temperatures below 50 K are explained well by the Gaussian line shape (fig.1(a)), whereas the Lorentzian line shape gives somewhat better agreement than the Gaussian one at higher temperatures(fig.1(b)). The QES spectra in YbP and YbAs also show the same features.

The important feature of the crossover from the Gaussian line shape to the Lorentzian one with the increase of temperature is clearly seen in the plot of the temperature dependence of a reliability parameter R. The R-factor is defined as follows;

\[
R = \sqrt{\frac{\sum (I_{i}^{\text{obs}} - I_{i}^{\text{cal}})^2}{\sum I_{i}^{\text{obs}}}}
\]

(1)

where \(I_{i}^{\text{obs(cal)}}\) indicates the intensity at the \(i\)th channel for an observed (a calculated) spectrum. Figure 2 shows the temperature dependence of the R-factors obtained by the Gaussian (open circles) and Lorentzian (closed circles) fitting for the three compounds. The lower dashed lines in fig.2 indicate statistical minimum values of the R-factors. It is quite remarkable that the crossover of QES spectra from the Gaussian line shape to the Lorentzian one is common for these compounds. The crossover temperature of about 150 K is also the same for these compounds.

Figure 3 shows the temperature dependence of the linewidths of the QES spectra (HWHM) in YbN (circles), YbP (squares) and YbAs (triangles) determined from the fitting procedure. Open and closed symbols indicate the results of the Gaussian and Lorentzian fittings, respectively. The data below 10K were taken with the triple axis spectrometer TOPAN with incident neutron energy of 14 meV. The results observed with TOPAN are consistent with those observed.

Fig.2 The R-factors for the Gaussian (open circles) and Lorentzian (closed circles) fits as a function of the temperature. The lower dashed lines indicate the statistical minimum values of the R-factors.
with LAM-D at higher temperatures. The results of the Lorentzian fitting below 50 K and those of the Gaussian fitting above 200 K are not shown in fig.3, because the QES spectra cannot be explained well by these line shapes. The observed linewidths of the QES spectra of these three compounds are almost the same, and increase with temperatures up to 50 K. They are almost constant or even decrease slightly above 150 K.

In order to discuss the temperature dependence of the linewidths in a common base independent of the spectral function, we introduce a 50 percentile width $\Gamma_0$ of the QES spectra as follows:

$$\int_{-\infty}^{\Gamma_0} S(\omega) d\omega = \frac{1}{2} \int_{-\infty}^{\infty} S(\omega) d\omega$$

(2)

where $S(\omega)$ is the QES spectral function. Figure 4 shows the obtained temperature dependence of the 50 percentile widths of YbN (circles), YbP (squares) and YbAs (triangles). Open and closed symbols indicate the results using the Gaussian and Lorentzian as the spectral function, respectively. It is noted that the 50 percentile widths of these three compounds change smoothly in spite of the crossover of the spectral shape function from the Gaussian type at low temperature region to the Lorentzian type at high temperature region.

We have also measured the momentum transfer ($Q$) dependence of the QES spectra in YbN at 10 K and at room temperature and in YbP at 1.5 K and at room temperature using TOPAN for $1.1 \text{ Å}^{-1} \leq Q \leq 1.7 \text{ Å}^{-1}$. Figure 5 shows the $Q$ dependence of the linewidth, HWHM, (a) and integrated intensity (b) of the QES spectra in YbN at 10 K. The dotted line in fig.5 (b) indicates the $Q$ dependence of the square of the magnetic form factor $f(Q)$ of the free Yb$^{3+}$ ion$^8$, which is scaled to the observed value at $1.31 \text{ Å}^{-1}$. From fig.5, we can conclude that the linewidth and integrated intensity in YbN are nearly independent of $Q$. We also observed the $Q$ independent feature of the QES spectra in YbP at 1.5 K. No appreciable $Q$ dependence of the QES spectra of either compound was observed at room temperature. Therefore, it is concluded that the spatial magnetic correlations between 4f electrons in these compounds are not strong enough to be detectable in powder samples.

Now, we discuss the nature of the magnetic fluctuations in the ground state $\Gamma_g$ in Yb monopnictides. Since the QES spectra are essentially the same for these three compounds, the magnetic fluctuations are concluded to be quite similar in YbX. This is consistent with the fact
that the bulk properties of YbX are also similar.

The Gaussian-like QES spectra at low temperatures indicate that the magnetic fluctuations at low temperature region are governed by the interatomic exchange interactions. The characteristic energy of the exchange interactions in these compounds is estimated to be about 20K from the linewidth at about 50K. It is considered that the big difference between the actual Néel temperature (~0.5K) and the estimated exchange energy (~20K) comes from the strong suppression of the magnetic ordering by the Kondo effect. Since the magnetic ordering is suppressed almost completely, the characteristic energy of the Kondo effect $T_K$ in YbX is suggested to be about the same value (~20K). This value of $T_K$ in YbX is about four times larger than the previously estimated value from the anomalous peak of the specific heat based on the impurity Kondo model.

The gradual change of the spectral line shape from Gaussian-like form to Lorentzian-like one with increasing temperature indicates that the single site relaxation process is not appreciable at low temperatures, but becomes important at high temperatures. The Lorentzian linewidth of 10K at room temperature is relatively small compared with those of the typical Kondo materials such as CeB$_6$, CeAl$_2$, or CeCu$_2$Si$_2$.[10] However, if the fact that the carrier density in YbX is very low is taken into account, c-f mixing effect in the YbX system should be rather strong compared with that in the typical Kondo materials.

References

NEUTRON SCATTERING STUDY OF Ce₃Au₃Sb₄

Mitsuo KASAYA, Kenichi KATOH, Masahumi KOHGI and Toyotaka OSAKABE

Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

ABSTRACT

Rare-earth compounds with an Y₃Au₃Sb₄-type crystal structure are semiconductors or semi-metals. Among them, Ce₃Au₃Sb₄ is a semiconductor with an activation energy of about 640 K and shows no magnetic order down to 1.5 K. The magnetic part of the specific heat for Ce₃Au₃Sb₄ obtained by subtracting the value for La₃Au₃Sb₄ from the total specific heat of Ce₃Au₃Sb₄ shows a broad peak at around 10 K, the origin of which is well explained by the crystalline-field splitting determined by neutron scattering.

INTRODUCTION

From our experimental studies of new rare earth compounds with an Y₃Au₃Sb₄-type crystal structure, we have found that La₃Au₃Sb₄ and Ce₃Au₃Sb₄ are narrow gap semiconductors and the valence of the Ce atom is a well-defined 3+ state¹ ². These experimental findings are also consistent with results of the band calculation on La₃Au₃Sb₄; the valence band comes mainly from the Sb-5p electrons and is filled by the transfer of three electrons from a La atom and one electron from an Au atom, leading La₃Au₃Sb₄ chemically to be La₃²⁺Au₃⁻Sb₄³⁻ and to be a semiconductor with an energy gap of 1900 K¹ ² ³. Then, the frame of the electronic structure of Ce₃Au₃Sb₄ may be the same as that of La₃Au₃Sb₄, but a localized 4f level is located within a filled valence band in the former. On the other hand, to study the mechanism of the appearance of Kondo resonance in Kondo insulators, theoretical studies have been performed from two extreme cases, i.e., one from nonmagnetic impurities, so-called Kondo holes, in Kondo insulator⁴, and the other from a single magnetic impurity in non-f nonmetallic system⁵ ⁶. Experimentally, however, systematic studies have not yet been done so far. In this sense, Ce₃Au₃Sb₄ is a good candidate for
the study of the structures within a band gap in Kondo insulator. Therefore, it is important to investigate the ground-state properties of Ce₃Au₃Sb₄ itself more in detail. In this paper, we will present the experimental results of the electrical resistivity and the specific heat of R₃Au₃Sb₄ (R=La, Ce, Pr, Sm, Gd). Then, we will mention about an anomaly of the specific heat observed in Ce₃Au₃Sb₄. Finally, we will show that this anomaly can be well explained by crystalline-field splitting determined by recent neutron scattering.

RESULTS AND DISCUSSION

First, we present the transport properties of non-f La₃Au₃Sb₄. As shown in Fig.1, La₃Au₃Sb₄ shows semiconducting behavior. Activation energy estimated above 200 K is 1540 K, which may correspond to the energy gap of La₃Au₃Sb₄, in agreement with the result of band calculation¹). As for the

![Fig.1. \(\rho(T)\) curves of R₃Au₃Sb₄ (after ref.2). Fig.2. \(\rho(T)\) curve of Ce₃Au₃Sb₄.](image)

heavier rare-earth members, Pr₃Au₃Sb₄ also shows semiconducting behavior, whereas Gd₃Au₃Sb₄ is metallic and the resistivity of the latter is two orders of magnitude smaller than that of the former. The present results indicate that R₃Au₃Sb₄ systems show a gradual evolution from semiconducting towards semi-metallic behavior as R is varied from La to Gd²). In Fig.2, we present temperature dependence of electrical resistivity of Ce₃Au₃Sb₄. The resistivity is 26 mΩ cm at room temperature and increases up to 4.5 Ω cm at 2 K and 15 Ω cm at 0.5 K²). The ratio of resistance \(R(0.5\,K)/R(300\,K)\) is 577. On the other hand, the temperature dependence of magnetic susceptibility \(\chi(T)\) above 150 K can be well described by the Curie-Weiss law with \(\Theta\), of 0.4 K and effective number of Bohr magneton of 2.45. The latter value is comparable with 2.54 for the free ions of Ce³⁺. This
result suggests that the valence of the Ce ions in Ce₃Au₃Sb₄ is 3⁺. These results are the reason why we consider the frame of the electronic structure of Ce₃Au₃Sb₄ to be the same as La₃Au₃Sb₄, with a 4f⁹ level in the filled valence band.

Next, we present experimental results of the specific heat C of R₃Au₃Sb₄. As is seen from Fig. 3, C of Sm₃Au₃Sb₄ and Gd₃Au₃Sb₄, show λ-type anomaly peaking at 2 and 10.3 K, respectively, which correspond to magnetic ordering temperatures. It is interesting to note that there is a minimum at about 3 K in the C(T) curve of Ce₃Au₃Sb₄; a sharp upturn in C/T is observed at low temperatures with C/T exceeding 2.5 J/mole K². The origin of this remains a future task. Another prominent feature is that the magnetic part of the specific heat of Ce₃Au₃Sb₄ obtained by subtracting the value for La₃Au₃Sb₄ from the total specific heat of Ce₃Au₃Sb₄, shows a broad peak at around 10 K. A plausible explanation is that the origin of it is that the peak comes from Schottky anomaly due to the crystalline-field splitting into three doublets, because local symmetry of rare-earth site in Y₃Au₃Sb₄-type structure is tetragonal 4 site.

![Fig. 3. Specific heat C vs T for R₃Au₃Sb₄ (R=La, Ce, Pr, Sm, Gd) (after ref. 2)](image)

In fact, the inverse magnetic susceptibility 1/ᵦ vs T curve deviates slightly from the Curie-Weiss law below 150 K¹¹ and we predicted that overall splitting of the J=5/2 state into three doublets by the crystalline field may be less than 150 K¹¹.

To determine the crystalline-field splitting of Ce₃Au₃Sb₄, we performed neutron scattering experiment by using the spectrometer LAM-D at the spallation neutron source KENS in the National Laboratory for High Energy Physics. Well-defined crystal field excitations were observed at 22 and 100 K. Crystal-field excitation levels are at 2.26, 10.37 and 12.47
meV. Based on the temperature dependence of the intensity, these excitations are attributed to be of magnetic origin and they correspond to crystalline-field transitions between the three doublets of Ce$^{3+}$ (J=5/2). Analysis of the specific heat by this crystalline field is shown in Fig. 4. Overall features of the magnetic specific heat are quite well explained by the crystalline field.

Fig. 4. Observed magnetic specific heat of Ce$_3$Au$_3$Sb$_4$ (open circles) and calculated one (solid line) based on the experimental results of neutron excitation (inset).

As is shown in Fig. 4, it is interesting to note that the magnetic specific heat increases below 3 K. To determine whether the upturn of the specific heat below 3 K is due to a Kondo resonance in a Kondo insulator or due to onset of magnetic ordering, elastic neutron scattering experiments are now in progress.

REFERENCES

2) K. Katoh and M. Kasaya, Physica B. in press.
7) N. Sato, private communication.
PHONON DISPERSION ANOMALY IN THE PREMARTENSITIC
$\beta_1$-PHASE AU-ZN ALLOYS

T. MAKITA, *A. NAGASAWA, °Y. MORII, °S. FUNAHASHI and H. OHNO

Office of Synchrotron Radiation Facility Project
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

*Department of Physics
Nara Women's University
Kitauoyanishi-machi, Nara-city 630 Japan

°Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

Transverse acoustic phonon dispersion relations along the [110] axis (e // [110]) in binary Au-Zn alloys were measured at 293, 150 and 110K by means of triple-axis neutron spectrometer installed in JRR-3M. Each dispersion relation curve was observed to have the anomalous dip. Phonon energy decreased with decreasing temperature. The effective interplaner force constants between the origin and $m$th neighbor atomic planes $\Phi_m$'s were determined through the least-squares fitting analysis on the phonon dispersion curves ($n=1$, 2 and 3). The $\Phi_2$'s were negative, while $\Phi_3$'s were positive. As temperature decreased, $\Phi_2$'s became smaller, but $\Phi_3$'s became larger. This means that the (110) planes of the second nearest neighbors are not coupled with each other, and the third nearest ones are strongly coupled. Thus the stacking structure with a periodic unit of three layers is considered to form. The dips appearing on the [110]TA1 phonon dispersion curves mainly originated from a characteristic combination of $\Phi_2$ and $\Phi_3$ in the $\beta_1$ phases. It was concluded that lattice dynamical precursor in the premartensitic $\beta_1$ state causes the change of $\Phi_2$ and $\Phi_3$.

INTRODUCTION

$\beta$ phase alloys of noble metals (Au, Ag, Cu) and divalent metals (Mg, Zn, Cd) are transformed to the ordered $\beta_1$ phases with structures of CsCl, Fe3Al and Heusler type ones by cooling or by rapid quenching. Usually the $\beta_1$ phases undergo the martensitic transformation by further cooling and/or under the stress field\textsuperscript{1}. The premartensitic $\beta_1$ states in $\beta$ phase alloys exhibit several kinds of anomalies. The typical one is the phonon dispersion anomaly that means usually a dip appears in the vicinity of the $2/3q_{max}$ or $q_{max}$ on the [110]TA1 phonon dispersion curve, where $q_{max}$ is the wave vector corresponding to the Brillouin zone boundary. [110]TA1 phonon corresponds with (110)[110] shear in martensitic transformation. The $\beta$ phase alloys that have so far been examined about phonon dispersion anomaly are ternary alloys of AuCuZn\textsuperscript{2-5}, Cu-Zn-Al\textsuperscript{6-7} and Cu-Al-Ni\textsuperscript{8}. Analyzing these phonon dispersion curves, we suggested that the phonon dispersion anomaly is not a precursor of a soft mode as had been observed, for example, in the displacive transformation in SrTiO\textsubscript{3}\textsuperscript{9}, but originates from a
characteristic combination of the interplanar force constants. With binary alloys, we have only known CuZn$^{10}$ and AgZn$^{11}$ alloys as \( \beta \) phase alloys. The former has a small anomaly, and the latter that has no martensitic transformation has no phonon dispersion anomaly. In order to confirm our idea on phonon dispersion anomaly and to understand physical properties in the \( \beta \) phase alloys systematically, neutron diffraction experiments were conducted on binary alloys simpler than ternary ones. In this paper, we deal with Au-Zn alloys.

**EXPERIMENTAL PROCEDURES**

In the present study, we have examined Au-48.5at.%Zn, Au-51.0at.%Zn and Au-51.5at.%Zn single crystal alloys. They were made from alloy ingots, which were prepared by melting together gold of 99.99 pct purity and zinc of 99.999 pct purity and then heat-treated for homogenization, by using the Bridgman method. The neutron diffraction experiments were performed on the specimens slowly cooled after annealing at 773K for 5 minutes.

For the neutron diffraction study, we used the triple axis spectrometer TAS-1 installed at JRR-3M in Tokai. Energy of incident neutron beams is selected by pyrolytic graphite monochromator. Tuned pyrolytic graphite filter was used to eliminate wavelength contamination. The four phonon dispersion branches of the Au-48.5at.%Zn were measured at room temperature by the incident neutron beams of 41.03 meV. The [110]TA\(_1\) phonon dispersion branches of the Au-51.5at.%Zn and Au-51.0at.%Zn were measured by the incident beams of 14.8 meV at three temperatures between room temperature and the martensitic transformation start temperature (Ms). Ms was determined in neutron powder diffraction method to measure the temperature when the diffraction pattern changed.

**RESULTS**

Figure 1 shows the four phonon dispersion branch curves of Au-48.5at.%Zn alloy at room temperature. We can see phonon dispersion anomaly on the TA\(_1\) branch.

Figures 2 and 3 show the phonon dispersion relations of the [110] TA\(_1\) branch of Au-51.5at.%Zn and Au-51.0at.%Zn alloy, respectively, at 293K (solid large circle), 150K (solid small circle) and 110K (open circle). The phonon energy decreased with decreasing temperature.

The Ms was 85 K and 75 K for Au-51.5at.%Zn and Au-51.0at.%Zn, respectively.

**DISCUSSION**

The binary AuZn alloys exhibited the phonon dispersion anomaly as same as in the ternary alloys. We analyzed the dispersion curve from the viewpoint of interplanar force constants. Concerning phonons propagating along the symmetry axes such as the [110] direction in the present case, the dispersion relation can be explained by a linear chain model. Here the interatomic force constant between the origin and \( n \)th neighbor (110) planes. The dispersion relation is then expressed as

\[
M \omega^2(q) = \sum_{n=1}^{N} \Phi_n (1 - \cos n \pi \frac{q}{q_{\text{max}}})
\]

where \( M \) is the reduced atomic mass, \( q_{\text{max}} \) is the wave vector corresponding to the [110] zone boundary, and \( \Phi_n \) is the interplanar force constant between origin and the \( n \)th neighbor (110) plane$^{12}$). Figure 4 is the results of the least-square fit equation (1) to the data on the Au-
Fig. 1 The phonon dispersion curves of Au-48.5at.\%Zn alloy at room temperature.

Fig. 2 The phonon dispersion relations of the [110]TA1 branch of Au-51.0at.\%Zn alloy, at 293K (solid large circle), 150K (solid small circle) and 110K (open circle).
Fig. 3 The phonon dispersion relations of the [110]TA1 branch of Au-51.5at.%Zn alloy, at 293K (solid large circle), 150K (solid small circle) and 110K (open circle).

Fig. 4 The analyzed result of the dispersion relation of Au-51.0at.%Zn by the least square fit to eq. (1).

51.0at.%Zn at 110K. Contributions from the first, second, and third terms are shown, respectively, as curves of n=1, 2, and 3.

The interplanar force constants $\Phi_2$ and $\Phi_3$ normalized by $\Phi_1$ are summarized in Table 1. As temperature decreased, $\Phi_2$'s became smaller, but $\Phi_3$'s became larger. This indicates that the (110) planes of the second nearest neighbors were not coupled with each other, and the third
nearest ones are strongly coupled. Thus the stacking structure with a periodic unit of three layers is considered to form. The dip appearing on the [110]TA1 phonon dispersion curve mainly originated from a characteristic combination of $\Phi_2$ and $\Phi_3$ in the $\beta_1$ phases. It was concluded that lattice dynamical precursor in the premartensitic $\beta_1$ state is thought to cause the changes of $\Phi_2$ and $\Phi_3$. This conclusion in the binary AuZn alloy agreed with those in ternary alloys.

<table>
<thead>
<tr>
<th>sample</th>
<th>Au-51.0at.%Zn</th>
<th>Au-51.5at.%Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>293K</td>
<td>150K</td>
</tr>
<tr>
<td>$\Phi_2/\Phi_1$</td>
<td>-0.259</td>
<td>-0.351</td>
</tr>
<tr>
<td>$\Phi_3/\Phi_1$</td>
<td>0.309</td>
<td>0.335</td>
</tr>
</tbody>
</table>

Table 1 The normalized interplanar force constants

ACKNOWLEDGMENTS

We thank Messrs. N.Minakawa and Y. Shimojyoh for their technical assistance in this research. The support received from the Department of Research Reactor Operation is gratefully acknowledged.

REFERENCES

STRUCTURAL PHASE TRANSITION AND SUPERCONDUCTIVITY
IN La$_2$-$_x$Ba$_x$CuO$_4$

*Susumu KATANO, *Satoru FUNAHASHI, *Jaime A. Fernandez-Baca,
#Nobuo MÔRI, #Chizuko MURAYAMA and #Yutaka UEDA

*Department of Physics, Japan Atomic Energy Research Institute
Tokai, Ibaraki 319-11, Japan

#Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831, USA

#The Institute for Solid State Physics, The University of Tokyo
Roppongi, Minato-ku, Tokyo 106, Japan

ABSTRACT

High-resolution neutron powder diffraction experiments and ac magnetic susceptibility measurements have been performed on La$_2$-$_x$Ba$_x$CuO$_4$ (x=0.125) at ambient pressure and under high pressures. Crystal parameters including bond lengths and angle are refined by profile analysis at ambient pressure. The results suggest that the changes in the Cu-O bonds accompanied with the structural phase transition may be related to the suppression of the superconductivity. The effects of pressure on the structural transition is fairly large. The LTT phase is greatly suppressed, and disappears at 0.7 GPa. The superconducting transition temperature T$_C$ remains almost constant up to 0.5 GPa; however, above this pressure it increases at the rate of about 10 K/GPa. These results clearly indicate a strong correlation between the crystal structure and the superconductivity in this system.

INTRODUCTION

The La$_2$-$_x$Ba$_x$CuO$_4$ system was discovered as the original high-T$_C$ superconductors,$^1$ and has been extensively studied. In recent years careful investigations of this system revealed that there exists a sharp dip in the T$_C$-x phase diagram; that is, the bulk superconductivity is greatly suppressed in the narrow range of x around 0.125.$^2,^3$ Subsequent studies of the
crystal structure clarified that the system undergoes com-plexed structural phase transitions. In the compound with \( x = 0.125 \), for example, the transition from the high-temperature tetragonal (HTT; space group \( I4/mmm \)) to the low-temperature orthorhombic phase (LTO; space group \( Bmab \)) takes place at about 200 K, and further the transition to the low-temperature tetragonal phase (LTT; space group \( P4_2/ncc \)) occurs at around 80 K.\(^4\) This structural transition to the LTT phase also appears in a narrow range of the Ba concentration \( x \). These results, hence, suggest that the superconductivity is suppressed in the region where the LTT phase shows up.

To elucidate the relation between the suppression of \( T_c \) and the structure phase transition, many efforts have been done. The substitution effects of \( Th^{4+} \) for \( La^{3+} \) indicated that the anomalous behavior in \( T_c \) is characterized by the hole density of \( 1/8 \) per Cu atom which is coupled with the LTT phase.\(^5\) Furthermore, the studies on \( Nd^{3+} \) substitution for \( La^{3+} \) in \( La_{2-x}Sr_xCuO_4 \) showed that this system induces another orthorhombic phase (LTO2; space group \( Pccn \)), and the superconductivity is modified by these structural phase transitions.\(^6\)

In order to get further information on the correlation between the superconductivity and the crystal structure in this system, high-resolution neutron powder diffraction and ac magnetic susceptibility measurements have been done on \( La_{2-x}Ba_xCuO_4 \) with \( x = 0.125 \) at ambient pressure and high pressures. The results have revealed new aspects in the structural and superconducting properties of this interesting system.

II. EXPERIMENTAL

The \( La_{2-x}Ba_xCuO_4 \) with \( x = 0.125 \) was prepared by solid-state reaction method of a mixture of predried \( La_2O_3 \), \( BaCO_3 \) and \( CuO \). The powders were pressed into a pellet, calcined at 900 °C for 24 h and then sintered at 1050 °C in air for several days with frequent grindings. The sample were finally annealed at 500 °C for 24 h in flowing \( O_2 \) gas.

Neutron diffraction experiments to study the crystal structure were made with the high-resolution powder diffractometer installed at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory. The \( (115) \) reflection of Ge was used as the monochromator. The neutron wavelength was \( 1.4000 \) Å. The data were collected with a 12’ inpile collimator, a 20’ monochromatic beam collimator and a 6’ diffracted beam collimator. The diffraction patterns at ambient pressure were obtained by a powder sample of about 3 cm\(^3\) using a Vanadium holder. The data obtained were analyzed by a Rietveld refinement program. For high-pressure experiments a clamp-type cell with a sapphire piston-cylinder was used.\(^7\) The pressure
medium was 3M Fluorinert liquid. The experiments under pressures were performed at 0.35 and 0.7 GPa. These measurements were carried out at temperatures down to 15 K using a standard closed-cycle refrigerator. The amount of the powder sample was limited by the size of the pressure cell, and the effective volume of the sample was about 0.3 cm$^3$. This limitation compounded with the high background scattering from the pressure cell made the diffraction experiments very difficult.

The superconducting transition temperature $T_c$ for this compound was examined under high pressures up to 2.5 GPa by ac induction method. The measurements were done using a clamp-type cell with a Teflon piston cylinder. The pressure medium was 3M Fluorinert liquid. The sample was cooled down to 2 K by pumping liquid $^4$He.

III. RESULTS AND DISCUSSION

In Fig. 1 neutron diffraction data at 115 K at ambient pressure are shown. These data were analyzed in the orthorhombic Bma$b$ space group (low-temperature orthorhombic: LTO). The data observed at 15 K showed that the reflections which split in the LTO phase become a sharp single peak. For this low temperature phase the symmetry of P4/nncm (tetragonal) and Pccn (orthorhombic) are proposed. However, the electron diffraction indicated that the tetragonal phase exists actually and this coexists with the orthorhombic phase whose orthorhombicity is quite small. Accordingly, even if the sample contains such a pseudo orthorhombic phase these two symmetry types cannot be distinguished. Hence the data were analyzed in the tetragonal P4/nncm symmetry.

FIG. 1. Diffraction pattern for La$_2$-$x$Ba$_x$CuO$_4$ with $x$=0.125 at 115 K. The data were analyzed by a Rietveld refinement program (Space group: Bma$b$). The solid line is the calculated profile. Tick marks show the positions of possible Bragg reflections.

Figure 2 and 3 show the bond lengths and angle of Cu-O as a function of Ba concentration. Here, O(1) and O(2) represent the oxygen atom on the Cu-O plane and the apical oxygen, re-
pectively. The diffraction data for the compounds except with \( x = 0.125 \) were analyzed in the orthorhombic Bmab structure. As shown in Fig. 2 the Cu-O bond lengths decrease almost linearly with \( x \), showing the increase in the hole density in the system. However, the changes in the Cu-O(1) at low temperature for \( x = 0.125 \), where the superconductivity is greatly suppressed, is rather small. Thus these changes in the bond lengths at \( x = 0.125 \) does not seem to explain the large decrease in the hole concentration at low temperatures; nevertheless, such changes indicate the distortion in the CuO\(_2\) plane, and would be one of the parameters which can be correlated with the suppression of \( T_c \). The changes in the Cu-O bond angle shown in Fig. 3 indicate that the tilt of the CuO\(_6\) octahedron decreases with increasing Ba concentration. For the compound with \( x = 0.125 \), this tilt angle is fairly enhanced at low temperature. These results could be correlated with the recent electronic structural consideration which showed that the density of states near \( E_F \) lowers somewhat in the LTT phase. Such a reduction of the density of states is due to the presence of two different sites for the planar O(1) in the LTT phase. The result suggests that an additional gap will be produced in the states in the charge transfer gap and may lead to the suppression of \( T_c \).

![Graph](image1)

FIG. 2. Bond lengths of Cu-planar O(1) and Cu-apical O(2) of La\(_{2-x}\)Ba\(_x\)CuO\(_4\) at 115 K (○) and 15 K (×) as a function of \( x \).

![Graph](image2)

FIG. 3. Bond angle Cu-O(1)-Cu of La\(_{2-x}\)Ba\(_x\)CuO\(_4\) at 115 K (○) and 15 K (×) as a function of \( x \).

Figure 4 shows the temperature dependence of the (2 2 0) reflection of the high-temperature tetragonal phase (HTT; I4/mmm) at ambient pressure. As the temperature is lowered from room temperature, this single peak starts to split below
about 202 K, indicating the transition to the low-temperature orthorhombic structure (LTO; Bmab). With decreasing the temperature further, the splitting becomes larger. Below around 78 K, however, a central component appears, and this shows a transition to another low temperature phase. At 70 K this peak becomes fairly sharp, and at 15 K it can be regarded almost as a single peak. Thus the sample in the present experiment shows an almost complete transition to the low-temperature tetragonal phase (LTT; P4$_2$/nmc) within the experimental accuracy.

The temperature dependence of the same reflection under 0.35 GPa indicates that the broadening of the peak, which shows the transition from the HTT to the LTO phase, starts at around 190 K, and it continues down to around 30 K. Below this temperature the central component appears; however, the peak is still broad even at 15 K. The result indicates that although the transition to the LTT phase takes place at around 30 K, the phase transition may not be complete even at 15 K and the sample might contain a small fraction of the LTO phase.

![Graph showing temperature dependence of neutron diffraction patterns for the tetragonal (2 2 0) reflection of La$_{2-x}$Ba$_x$CuO$_4$ with x=0.125 at ambient pressure. The data are fitted with one or two Gaussians.](Image)

**FIG. 4.** Temperature dependence of neutron diffraction patterns for the tetragonal (2 2 0) reflection of La$_{2-x}$Ba$_x$CuO$_4$ with x=0.125 at ambient pressure. The data are fitted with one or two Gaussians.

![Graph showing temperature dependence of neutron diffraction patterns for the tetragonal (2 2 0) reflection of La$_{2-x}$Ba$_x$CuO$_4$ with x=0.125 under 0.7 GPa. The data are fitted with one or two Gaussians.](Image)

**Fig. 5.** Temperature dependence of neutron diffraction patterns for the tetragonal (2 2 0) reflection of La$_{2-x}$Ba$_x$CuO$_4$ with x=0.125 under 0.7 GPa. The data are fitted with one or two Gaussians.
Diffraction data under 0.7 GPa is shown in Fig. 5. The transition temperature between the HTT and LTO phase estimated by the broadening of the peak is about 183 K. When the temperature is lowered the split of the peak becomes clear. Under this pressure, however, the appearance of the central component is not clearly observed down to 15 K. Thus, the transition to the LTT phase in this compound disappears under a pressure below 0.7 GPa.

The results obtained in the present experiment show that the effect of pressure on the LTO-LTT transition is quite large and the orthorhombic phase is stabilized under high pressure. From these results pressure coefficient of the transition temperature for the HTT-LTO phase transition is obtained to be $-28 \pm 6$ K/GPa, and that of the LTO-LTT transition is $-135 \pm 10$ K (GPa). The value for the former transition is rather small, and is just about 1/4 of that in the $(La,Sr)_{2}CuO_{4}$ system. The latter for the transition to the LTT phase, on the other hand, is quite large. The low-temperature tetragonal structure disappears under pressure of about 0.6 GPa.

The pressure dependence of $T_{c}$ obtained by magnetic susceptibility measurements are shown in Fig. 6. As was observed in careful investigations, the diamagnetic susceptibility at ambient pressure shows the two-step superconducting transition. The first component is a trace of the superconductivity at around 30 K. This would be due to the presence of a small fraction of the LTO phase. As shown in the diffraction patterns at low temperatures, however, the volume of this phase is so small that the phase is inconspicuous in the diffraction data. The transition temperature to this superconductivity increases under pressures. The second component is a bulk transition observed at about 4 K. As the magnetic susceptibility shows the volume fraction of this bulk superconductivity is also fairly small (a few percent) at ambient pressure. Under high pressures up to 0.5 GPa, the behavior of the susceptibility does not change large: the superconducting transition temperature remains almost constant. However, above 0.6 GPa the bulk superconductivity is greatly enhanced. Both $T_{c}$ and the volume fraction of the superconductivity fairly increase with pressure up to about 1.5 GPa. These values, however, saturate above this pressure.

As shown in Fig. 6, the transition temperature for the trace of the superconductivity at higher temperatures increases at the rate of 7 (±2) K/GPa, and saturates at around 2 GPa. On the other hand, the transition to the bulk superconductivity does not change up to 0.5 GPa; above this pressure, however, $T_{c}$ increases greatly at the rate of 10 (±2) K/GPa. At around 1.5 GPa the transition temperature saturates, and then decreases a little. These pressure coefficients obtained here are two or three times larger than those for the Sr substituted
system. Since the Sr substitution does not induce the LTO-LTT phase transition, such large values might be related with the structural phase transition of the present system. In the figure, the transition line between the LTO and LTT phase is shown in the broken line. From this figure it is apparent that the bulk $T_C$ is greatly enhanced when the LTT phase disappears under high pressures. The results clearly show a correlation between the suppression of the bulk superconductivity and the structural transition to the LTT phase.

As mentioned above, the bulk $T_C$ remains around 15 K even at the highest pressure of 2.5 GPa, and does not reach the value of about 30 - 40 K. This might suggest that the electronic structure of the orthorhombic (LTO) phase stabilized by pressure is still complicated in this particular compound with the hole density of $1/8$. The density of states at the Fermi level (i.e. the density of holes which are responsible for the superconductivity) may be lower than that of the LTO phase in the 30 K superconductors. As the other possibility, the following may be pointed out. In the experiments for the La$_{1.88-x}$Nd$_x$Sn$_{0.12}$CuO$_4$ system, the Nd substitution induces the structural change from the LTO to another orthorhombic Pccn and then to the LTT phase; further, in this structure sequence $T_C$ decreases systematically. The transition temperature around 15 K observed in the Pccn phase of this system corresponds with $T_C$ which is obtained under high pressure. Hence, if the same relation between the structure and $T_C$ exists in the present system, the structure induced under pressure may be Pccn. Although the transition to the orthorhombic Pccn under high pressure is not clear in the data under 0.7 GPa within experi-
mental uncertainty, it may be possible that pressure induces such an intermediate orthorhombic structure rather than it changes the structure to the LTO phase directly. To make clear whether the Fccn structure is induced or not, more detailed experiments under high pressures will be necessary.

In conclusion, pressure effects on the structural phase transition in La$_2$xBaxCuO$_4$ with $x=0.125$ have been investigated directly by neutron diffraction. The transition temperatures both of HTT-LTO and of LTO-LTT increase with pressure. The large suppression of the LTT phase under high pressure is particularly noted. The two-step transition to the superconducting states is observed even under high pressures. The results show that the bulk superconductivity restores greatly when the LTT phase disappears under high pressure. There exists a strong correlation between $T_C$ and the crystal structure in this system.

ACKNOWLEDGMENTS

The neutron diffraction experiments were carried out at the Oak Ridge National Laboratory under the U.S. - Japan Cooperative Program on Neutron Scattering. The Oak Ridge National Laboratory is managed by Martin Marietta Energy Systems, Inc. for the Division of Materials Science of the U.S. Department of Energy under Contract No. DE-AC05-84OR21400.

References

Diffraction Study on the Nonstoichiometric $\alpha$-U$_2$N$_{5+x}$ Phase

H. Serizawa, K. Fukuda, Y. Ishii, S. Funahashi

Japan Atomic Energy Research Institute, Tokai-mura, Naka-Gun, Ibaraki-Ken, 319-11 Japan

and

M. Katsura

Osaka University, Department of Nuclear Engineering, Faculty of Engineering, Yamadaoka 2-1, Suita, Osaka, 565 Japan

Abstract

X-ray and neutron diffraction studies were performed on nonstoichiometric $\alpha$-U$_2$N$_{5+x}$ having a composition range $1.68 < N/U < 1.84$. It was confirmed that the crystal structure of $\alpha$-U$_2$N$_{5+x}$ in this composition range was distorted Mn$_2$O$_3$-type. Structure parameters of U and N atoms were determined. The results showed that positions of U atoms varied continuously with nitrogen content. No evidence of the modification from bcc to fcc could be obtained. Interatomic distances of U–U and U–N were determined. The position parameter of N atoms showed that N atoms were slightly deviated from the tetrahedral site.

I. Introduction

In U–N system, there are two sesquinitrides, which are named as $\beta$–U$_2$N$_3$ and $\alpha$–U$_2$N$_3$. The crystal structure of $\beta$–U$_2$N$_3$ formed at temperatures higher than 800 °C is hexagonal with La$_2$O$_3$–type structure. The other sesquinitride, $\alpha$–U$_2$N$_3$, is indexed as body-centered cubic with Mn$_2$O$_3$–type structure, and exhibits a wide range of composition by dissolving nitrogen in N vacant site, so that its formula is denoted as $\alpha$–U$_2$N$_{3+x}$. Although the other nitride, U$_4$N$_7$, with CaF$_2$–type structure was reported [1], the existence is still in question. It is well known that the lattice constant and X-ray diffraction pattern of $\alpha$–U$_2$N$_{3+x}$ vary with its composition. These variations seem to indicate some phase transition which may occur with dissolving nitrogen in the $\alpha$–U$_2$N$_{3+x}$ phase.

Several works on the phase transition have been reported, in which two predictions were proposed on it so far. Rundle et al. [2] and Anselin [3] analyzed $\alpha$–U$_2$N$_{3+x}$ phase by X-ray diffraction (XRD) in the composition range, $1.435 < N/U < 1.75$, and suggested that the crystal structure of $\alpha$–U$_2$N$_{3+x}$ should be modified continuously from $\alpha$–U$_2$N$_{3+x}$ with Mn$_2$O$_3$–type bcc
structure toward CaF$_2$-type fcc structure with increasing the nitrogen content. On the other hand, Tobisch and Hase [4], and Masaki et al. [1] reported that such a phase transition could not be found. In order to clarify the phase transition, on which there are contradictive predictions, it is necessary to perform the crystallographic study on nitrogen-rich α-U$_2$N$_{3+x}$ phase (N/U>1.75). We have, therefore, undertaken X-ray and neutron powder diffraction studies on α-U$_2$N$_{3+x}$ with a wide composition range. The diffraction data were refined by means of RIETAN-program [5] to obtain variations of position parameters and occupation factors of U and N atoms. We also calculated interatomic distances (U–U and U–N) which would provide the useful information for the thermodynamic property of the phase.

2. Experimental

All samples of α-U$_2$N$_{3+x}$ were prepared from high-purity uranium metal. The metal was converted to UH$_3$ powder through a heat treatment with hydrogen, which was purified by flowing through a liquid nitrogen trap. The nitrogen-rich α-U$_2$N$_{3+x}$ (N/U>1.75) was prepared by the reaction of UH$_3$ and a gas mixture of ammonia, hydrogen and nitrogen at 400°C. The composition of the product could be controlled by changing the mixing ratio of the three gases. The products were then quickly cooled and stored in vacuum, since α-U$_2$N$_{3+x}$ obtained in this way is easily oxidized in the air. The nitrogen-poor α-U$_2$N$_{3+x}$ (N/U<1.75) were obtained by heat treatments of UH$_3$ at 800 °C and 1000 °C in dried nitrogen atmosphere of 1 atm for 72 hours. The samples for X-ray and neutron diffraction analyses were prepared in a glove-box with a high-purity argon atmosphere (oxygen concentration <10 ppm). The chemical analyses were carried out on three samples with high nitrogen content. The nitrogen content of the sample was determined by a modified Kjeldahl method developed by Handa et al. [6]. The oxygen contained as impurity in the sample was determined by an inert gas fusion-coulometry [7].

Results of the chemical analyses are presented in Table 1 together with corresponding lattice constants. The XRD patterns showed that the samples were composed of a single phase. Although oxygen detected by the chemical analysis should exist as UO$_2$, no trace of the phase was recognized by the XRD analysis. We, therefore, disregarded the presence of oxygen in the following discussions.

The XRD analyses were made at room temperature using a diffractometer (rotating anode X-ray tube type, RU-200B, Rigaku Co. Ltd.) with CuK$_\alpha$ radiation monochromated by (002) plane of graphite. The measurements on the samples were conducted with stepwise scanning from 15° to 125° at intervals of 0.05° for a duration of 7 seconds.

The neutron diffraction patterns were taken with a neutron wave length of 0.18225 nm at room temperature by the High Resolution Powder Diffractometer (HRPD) installed in the

| Table 1 Results of chemical analyses of α-U$_2$N$_{3+x}$ |
|-----------------|----------------|-------------|-----------|-------------|
| Sample name     | Nitrogen (wt%) | Oxygen (wt%) | N/U ratio | Lattice constant (nm) |
| SAMPLE-1        | 9.77±0.08      | 0.2±0.1     | 1.83      | 1.0594      |
| SAMPLE-2        | 9.77±0.04      | 0.4±0.1     | 1.83      | 1.0600      |
| SAMPLE-3        | 9.69±0.05      | 0.3±0.1     | 1.82      | 1.0596      |

— 523 —
3. Results and Discussion

3.1 Relationship between nitrogen content and lattice constant

The composition dependence of the lattice constant was reported previously by other workers [2, 3, 8-15]. The relationship between the lattice constant and N/U atomic ratio for α-U$_2$N$_{3+x}$ is plotted in Fig. 1, where a dotted line and a solid line were reported by Tagawa and Masaki [10], and GMELIN handbook [15], respectively. The solid line in the figure suggest the continuous phase transition from bcc to fcc. While, an existence of discrepancy and slope change of the dotted line at N/U=1.75 implies the discrete transformation from α-U$_2$N$_{3+x}$ with Mn$_2$O$_3$-type structure to U$_4$N$_7$ with CaF$_2$-type structure at the composition [10].

The data of the chemical analysis and XRD obtained in the present work are consistent with those expressed by the solid line. As described above, this result suggests the phase transition should occur continuously.

3.2 Information on displacements of U atoms in the unit cell

Typical XRD patterns of both of nitrogen-rich and -poor α-U$_2$N$_{3+x}$ obtained in the present study were given in Fig.2. Weak peaks are reflections being characteristic of a bixbyte-type (bcc) lattice, which corresponds to Mn$_2$O$_3$-type structure. It should be noted that the intensity of each weak reflection which can be seen in the pattern of nitrogen-poor α-U$_2$N$_{3+x}$ decreased in the pattern of nitrogen-rich α-U$_2$N$_{3+x}$, but those peaks did not disappear completely. This is one of the evidence that the crystal structure of nitrogen-rich α-U$_2$N$_{3+x}$ is still keeping bcc structure in space group Ia3 which is the same as that of nitrogen-poor α-U$_2$N$_{3+x}$.
Consequently, it may be concluded to consider that phase transition which was suggested by Masaki et al.[1] would not occur in \( \alpha\text{-U}_2\text{N}_{3\text{x}} \) phase. XRD patterns were refined with the RIETAN-program by a FACOM large scale computer[5]. The discrepancy index, \( R_f \text{(structure factor R-factor), which was defined as} \)

\[
R_f = \frac{\Sigma_k \left| I_k('o') - I_k('c') \right|}{\Sigma_k I_k('o')}
\]

for the refinements, for each refinement was less than 6, where \( I_k('o') \) is the integrated intensity evaluated from a summation of contributions of \( k\text{-th} \) peak to net observed intensities, and \( I_k('c') \) denotes the integrated intensity calculated from refined structure parameters.

\( \alpha\text{-U}_2\text{N}_{3\text{x}} \) contains 32 U atoms in its unit cell, where U atoms occupy 8(b) and 24(d) sites in space group Ia3 [16]; we designate U atoms at 8(b) and 24(d) sites as U(1) and U(2), respectively.

![Fig. 3 Variations of position parameters of U(1) (U atoms at 8(b) site)](image3)

![Fig. 4 Variations of position parameters of U(2) (U atoms at 24(d) site)](image4)

The atomic scattering factor of N atom for X-ray was negligibly small, so that the effect of N atom on the position parameters of U atoms could be neglected.

Variations of the position parameters of U(1) and U(2) with increasing nitrogen content are given in Figs. 3 and 4, respectively. The composition for each specimen in the Figs. 3 and 4 was estimated with the lattice constant by referring the solid line in Fig. 1. A marked tendency was observed as follows; in the lower nitride region (N/U<1.75), the position parameters of U(1) and U(2) did not vary steeply with increasing nitrogen content. Figures 3 and 4 indicate that U(1) and U(2) shift toward \(<0,-1,-1>\) and \(<1,1,-1>\), respectively. Figure 3 shows that displacement of U(1) along X-axis is small compared with those along Y and Z-axes. Figure 4 shows that U(2) shifts with composition change, and traverse \((0, 1, 0)\) plane in the vicinity of the composition N/U=1.82. The displacement of U(2) along the X-axis was also recognized, but that along Z-axis was scarcely changed. When the crystal structure of
\( \alpha-U_2N_{3-x} \) is modified from bcc to fcc with increasing nitrogen content, the position parameters of \( U(1) \) and \( U(2) \) should approach those expressed by open symbols in Figs. 3 and 4. However, in these figures, the variations of the position parameters did not show such tendency.

Using the numerical values of the lattice constant and the position parameters, we calculated the interatomic distance between \( U(1) \) and \( U(2) \). Variation of the interatomic distance is given as a function of the composition in Fig. 5. The interatomic distance decreases rapidly with increasing nitrogen content. The dotted line in the figure denotes the calculated distances on the assumption that the displacement of \( U \) atoms is neglected even if the nitrogen content changes. The difference between the experimental data and the calculated line indicates that the displacement of \( U \) atoms in the unit cell cannot be neglected to elucidate the interatomic distances.

**3.3 Information on nitrogen dissolved in the unit cell**

The neutron diffraction analysis reveals the positions of \( N \) atoms dissolved in \( \alpha-U_2N_{3-x} \). Some information on the position parameters and occupation factors of \( N \) atoms for nitrogen-poor \( \alpha-U_2N_{3-x} \) were provided by Tobisch and Hase [4], and Masaki and Tagawa [11]. The \( N \) atoms in nitrogen-poor \( \alpha-U_2N_{3-x} \) occupy at 16(c) and 48(e) in the space group Ia3; we denote \( N \) atoms in the positions of 16(c) and 48(e) as \( N(1) \) and \( N(2) \), respectively. The neutron diffraction patterns obtained in the present study are shown in Fig. 6. These patterns were also refined by using RIETAN program. The \( R_f \) values for the refinement of the diffraction patterns of the samples with the composition, \( N/U=1.82 \) and 1.73 were 5.36 and 6.17, respectively. The position parameters of \( U \) atoms which had been determined in the XRD study were used in this refinement. The position parameters and occupation factors of \( N \) atoms.
obtained in the present study are summarized in Table 2 together with the previous results. N/U atom ratio in the table was estimated from the lattice constant. The occupation factors of N atoms in nitrogen-poor \( \alpha-U_2N_{3+x} \) (N/U = 1.73) agree well with those of the previous works [4, 11]. The composition dependence of the occupation factor at 16(C) site listed in Table 2 shows that the factor increases with the composition. Therefore, it is evident that excess N atoms occupy the position of 16(c) predominantly. Although the presence of empty sites in a small part of the position 48(e) was suggested in nitrogen-rich \( \alpha-U_2N_{3+x} \), the occupation factor was larger than that at 16(c) site. The difference in the occupation factors would express an inequivalence between these two positions, 16(c) and 48(e) sites. If nitrogen-rich \( \alpha-U_2N_{3+x} \) was CaF\(_2\)-type structure, these two positions were to be equivalent. Then, this result also means that nitrogen-rich \( \alpha-U_2N_{3+x} \) should be crystallized as Mn\(_2\)O\(_3\)-type structure.

A part of the unit cell of \( \alpha-U_2N_{3+x} \) is drawn in Fig. 7. Both of N(1) and N(2) have the four nearest neighboring U atoms. The interatomic distances between U atom and N atom in \( \alpha-U_2N_{3+x} \) are summarized in Table 3. Symbols in the second and third columns in the table correspond to atoms appearing in Fig. 7. The mean error was about 0.003 nm. As seen in Table 3, in nitrogen-poor \( \alpha-U_2N_{3+x} \), the interatomic distances between N atom and three U atoms (\( \gamma, \beta, \delta \) for N(1) and \( \xi, \eta, \delta \) for N(2)) among neighboring four U atoms were nearly the same, and the distance between the N atoms and the rest of neighboring U atom was larger than above three values, meaning that the positions of N atom deviate from the tetrahedral site. The interatomic distances between N atom and U atom in the

Table 2 Position parameters and occupation factors of N atoms in \( \alpha-U_2N_{3+x} \)

<table>
<thead>
<tr>
<th>U(1) Position</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>Occupation Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>16(a)</td>
<td>0.116±0.015</td>
<td>0.115±0.015</td>
<td>0.113±0.015</td>
<td>1.00</td>
</tr>
<tr>
<td>16(b)</td>
<td>0.115±0.015</td>
<td>0.115±0.015</td>
<td>0.115±0.015</td>
<td>1.00</td>
</tr>
<tr>
<td>16(c)</td>
<td>0.116±0.015</td>
<td>0.116±0.015</td>
<td>0.116±0.015</td>
<td>1.00</td>
</tr>
<tr>
<td>16(d)</td>
<td>0.117±0.015</td>
<td>0.117±0.015</td>
<td>0.117±0.015</td>
<td>1.00</td>
</tr>
</tbody>
</table>

* Teich and Ham ** Mochi and Tegawa

Fig. 7 Arrangement of U and N atoms in bixbyte-type structure

---

527
composition range from N/U=1.73 to 1.82 did not depend on the composition.

5. Summary

1) U atoms in α-U$_2$N$_{3+x}$ displaced continuously with increasing nitrogen content. The pronounced displacement was observed in nitrogen-rich α-U$_2$N$_{3+x}$ phase. However, any modifications, such as the formation of other nitrides (UN$_2$ or U$_4$N$_7$), were not observed. A specimen in nitrogen-rich α-U$_2$N$_{3+x}$ phase examined in the present study was crystallized Mn$_2$O$_3$-type structure which is the same as that of nitrogen-poor α-U$_2$N$_{3+x}$ phase.

2) The interatomic distance between U(1) and U(2) decreased steeply with increasing nitrogen content.

3) The position of excess nitrogen dissolved in α-U$_2$N$_{3+x}$ phase was confirmed. The excess nitrogen atoms were located predominantly at the position 16(c). In nitrogen-rich α-U$_2$N$_{3+x}$, the presence of the empty site in the position 48(e) was suggested.

4) The position of N atoms in α-U$_2$N$_{3+x}$ were shifted from their tetrahedral site.

References

Acknowledgements

The authors wish to express their thanks to Mr. Y. Shimojo, for his technical supports in the neutron diffraction study. Thanks are also due to Mr. A. Maeda and Mr. K. Shiozawa who assisted the chemical analyses. The authors are indebted to Drs. T. Kondo, and M. Handa for their interest and encouragement in the present work.
COOLING PROCESS DEPENDENCE OF SPIN STRUCTURE IN THE REENTRANT SPIN GLASS Fe$_{0.715}$Al$_{0.285}$

J. SUZUKI, *H. R. CHILD, +M. ARAI and #Y. ENDOH

Department of Physics, Japan Atomic Energy Research Institute
Tokai, Naka 319-11, Japan

*Solid State Division, Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831, USA

+Faculty of Science, Kobe University
Rokkodai, Nada, Kobe 657, Japan

#Faculty of Science, Tohoku University
Aramaki, Aoba, Sendai 980, Japan

In spin glass system the existence of irreversibility below spin glass temperature is well known with magnetization measurement. However, it is not realized how the irreversibility is affected by spin structure. Neutron scattering experiments were performed on the reentrant spin glass alloy Fe$_{0.715}$Al$_{0.285}$ in a few different kinds of cooling processes: ZFC (Zero Field Cooling), FC (Field Cooling) and NF (No Field). All the data was collected with the Wide Angle Neutron Diffractometer (WAND) installed in the Oak Ridge National Laboratory. The weak magnetic field of 60 Oe was applied in the direction perpendicular to wave vector change in both the ZFC and the FC. Especially, in the ZFC the measurement was performed within a short period to avoid the variation of the spin structure with the advance of magnetic relaxation under the field. Changes of the scattering pattern in these cooling processes appeared just around nuclear Bragg peaks. The peak intensity at the Bragg points in the FC was higher than that in the ZFC. Furthermore, the peak width in the former was narrower than that in the latter. On the other hand, the scattering pattern in the NF was almost the same in the ZFC. These results suggest that all the spin components parallel to the field is uniformly induced in the FC and spin glass state in the NF is considerably stable for the applied field.
Lithium oxide (Li$_2$O) has the antifluorite structure in which oxygen ions are in a fcc sublattice and lithium ions are in a simple cubic sublattice. Li$_2$O is a kind of super ionic conductor and lithium ion is very mobile above 500K. This behavior affects on the mechanical and the electrical properties of Li$_2$O. To understand the fundamentals such as the vibration amplitude, the dynamical force constants and the frequency distribution of Li$_2$O, elastic and inelastic neutron scattering studies on 7Li$_2$O was carried out by the high-resolution powder diffractometer and the triple-axis neutron spectrometers. Intensity of the Bragg peaks of Li$_2$O was measured in the temperature range from 300K to 1120K. From an analysis of the temperature dependence of the Bragg intensities of Li$_2$O, we found that oxygen ions vibrate harmonically in this temperature range, but lithium ions vibrate anharmonically above 400K. To clarify the anharmonic thermal vibration of lithium ions, inelastic neutron scattering experiment was carried out at 300K and 700K. Phonon energy was measured by an energy loss and a constant-q method. In a triple degenerated mode at q=0, oxygen atom is at rest and two lithium atoms vibrate in anti-phase. Phonon energies of this mode at 300K and 700K were 65meV and 58meV, respectively. On the other hand, in the mode in which two lithium ions vibrate in phase and move in anti-phase to oxygen ion, difference of the phonon energies measured at 300K and 700K was very small. Therefore, the temperature dependence of the force constant between lithium ions was larger than that of another force constants in Li$_2$O.
REFINEMENT OF PHONON EIGENVECTOR PHASES FROM INTENSITIES OF NEUTRON INELASTIC SCATTERING IN Si.

1Jiri KULDA, 2Dieter STRAUCH and 3Yoshinobu ISHII

1 Institut Laue-Langevin, 156x, 38042 Grenoble Cedex, France
and
Nuclear Physics Institute, 25068 Rez near Prague, CR

2 Institut f. theoretische Physik, Universität Regensburg, FRG

3 Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT.

The [111] direction in diamond structure is one of the simplest cases where the phonon polarization vectors are not fully determined by symmetry. For the longitudinal phonons there appears a phase shift between the motions of the two sublattices which can be observed only via the intensities of neutron coherent inelastic scattering. In order to minimize experimental errors in their determination we have employed a new strategy, analogous to those utilized in crystallography: we have measured at a given energy transfer the intensities due to two different longitudinal acoustic phonon branches ([00ξ] and [ξξξ]) in various Brillouin zones and the unknown phase was then refined together with a scale factor from the observed inelastic structure factors. When comparing the resulting phase variation within a Brillouin zone with the prediction of the bond charge model calculations a slight deviation is found at ξ>0.25 which may stimulate further theoretical work.
INTRODUCTION

The phonon dispersion relation \( \omega(q) \) itself does not provide complete information on the lattice dynamics of a given crystal unless there is a single atom per unit cell. This follows from the mathematical structure of the dynamical matrix \( D(q) \).\(^1\),\(^2\) The importance of knowledge of the polarization vectors describing the mutual movement of different atoms in a given mode has been recognized since the early days of investigation of lattice dynamics and several attempts to interpretate the intensities of neutron coherent inelastic scattering in this sense have been reported.\(^3\),\(^4\),\(^5\) This task although conceptually straightforward and analogous to the current practice in X-ray and neutron crystallography is in reality much more complicated. The inelastic intensities are related to a curved scattering surface rather than a point in the \((Q, \omega)\) space so that observed count rate is sensitive not only to the particular size of the resolution ellipsoid but also to its shape and orientation. Moreover, during the usual \( Q = \text{const.} \) scans either incident or scattered wavelength is changed leading to variations of the resolution function. These factors, accompanied by a frequent presence of spurious peaks, complicate the quantitative evaluation of observed intensities immensely. It appears that procedures, developed for normalization of observed intensities\(^6\) and providing reliable results as far as line positions only are requested, may fail to some extent if intensities due to different modes are compared: both Iizumi\(^4\) working on CaF\(_2\) and more recently Strauch et al\(^5\) on silicon have found significant departures from rules quoting that sum of intensities scattered by LA/LO modes at a given point in Brillouin zone should be constant. However, these departures may originate not only from inadequacies in account of resolution effects but also from violations of the first Born approximation (kinematic approach) in description of the scattering process itself.

In the present work we adopted a different procedure consisting in measurement of intensities due to phonons at some fixed energy transfer in several Brillouin zones and in a subsequent refinement of the unknown parameter together with a common scale factor from such a data set in order to minimize the influence of instrumental corrections. As well we decided to verify the kinematic behaviour of the observed intensities - i.e. their proportionality to the square of structure factor and to thickness of the sample. Silicon was chosen as a most suitable material because samples of a well defined quality can easily be prepared in any shape and size and results of a quite recent experiment of the same type are available for comparison.
THEORY.

The displacement $\vec{u}(l,k)$ of the $k$th atom in $l$th cell can be written in terms of a sum over all phonon wave vectors and modes $j$ as\(^{5}\)

$$\vec{u}(l,k) = \sum_{q,j} \sqrt{\frac{\hbar}{2\omega(q,j)NM_k}} \vec{e}(k|q,j) \exp[i\vec{q} \vec{R}(l)](\hat{a}_{q,j} - \hat{a}_{q,j}^+)$$

where $N$ and $M_k$ are the number of atoms per unit volume and the atomic mass, respectively, $\vec{e}(k|q,j)$ denotes the phonon polarization vector and $\hat{a}_{q,j}$, $\hat{a}_{q,j}^+$ are the creation/annihilation operators. Sometimes a slightly different convention is used for the eigenvector phases, putting

$$\vec{u}(l,k) = \sum_{q,j} \vec{e}(k|q,j) \exp[i\vec{q} \vec{r}(l,k)](\hat{a}_{q,j} - \hat{a}_{q,j}^+)$$

where $\vec{r}(l,k) = \vec{R}(l) + \vec{d}(k)$ and $\vec{d}(k)$ is the position vector of the $k$th atom with respect to the unit cell origin. Obviously the polarization vectors differ by a phase factor $\exp[i\vec{q} \vec{d}(k)]$. In what follows we shall denote the phases corresponding to the $\vec{e}$ and $\vec{e}$ conventions by $\phi$ and $\Phi$, respectively, with

$$\phi(q) = \Phi(q) + q \vec{d}(k)$$

In the diamond structure the primitive cell contains two types of atoms positioned at the origin and at $\frac{\alpha}{4}[111]$, respectively. The polarization vectors for the LA modes in the $\Delta$ and $\Lambda$ directions can be written as

$$\vec{e}(1|q) = \bar{e}_1 = \frac{1}{\sqrt{3}}[111]$$

and

$$\vec{e}(2|q) = \bar{e}_2 \exp[i\phi(q,j)].$$

The relation between the corresponding phases becomes

$$\Phi(\xi) = \phi(\xi) = -\frac{3}{2} \pi \xi.$$ (4)

The experimentally observed intensities can be expressed as

$$I_{obs} = \frac{V}{v_0} (\bar{Q} e)^2 \frac{\langle n + 1 \rangle \hbar}{2M\omega(q)} \exp[-2W(Q)] \frac{1}{v_q \cos \chi} f(Q)^2$$

(5)
where all the symbols have their usual meaning and \((v_s \cos \chi)^{-1}\) is the Jacobian corresponding to the E=const scans\(^7\) with \(v_s\) and \(\chi\) being the phonon group velocity and the angle between scan direction and \(\tilde{\nabla}_q \omega\); in our case always \(\chi=0\). The eigenvector phases enter the observed intensities through the inelastic structure factors which for the present purpose can be written as

\[
f(\tilde{\tau} + \tilde{q}) = f_0 \left| 1 + \exp \left[ i(\tilde{\tau} \tilde{d}_2 - \Phi(\tilde{q})) \right] \right|
\]

where \(f_0\) is a scale factor and \(\tilde{\tau} \tilde{d}_2\) equals a multiple of \(\pi/2\) depending on the Brillouin zone indices.

**EXPERIMENTAL RESULTS.**

The neutron measurements were performed at the JRR-3 reactor (20 MW, 3\times10^{14} \text{ n cm}^{-2}\text{s}^{-1}) at the Japan Atomic Energy Research Institute (JAERI) on the TAS-1 three axis spectrometer. Pyrolytic graphite (002) and (004) reflection were used on the monochromator and analyzer, respectively, together with beam collimations 40'-20'-40'-40'. The final neutron momentum was fixed throughout all the experiments at \(k_f = 4.482 \ \text{Å}^{-1} (E_f = 10 \text{THz})\).

The samples were prepared from zone melted, low doped, dislocation-free silicon single crystal ingots grown in the [100] and [111] directions. Several plane-parallel plates of different thicknesses (1 to 15 mm) and surface orientations were cut on diamond saw and the damaged surface layer was etched down (=10 \(\mu\)m). In the final stage of the intensity measurement samples cca 5 mm thick were used.

As one possible reason for departures from the sum rules for intensities might have been some interference effect or multiple scattering violating the proportionality of the intensities to the sample volume and to the square of the structure factor we have performed two experimental checks of formula (5). First, in a complementary experiment on the TAS-2 spectrometer we verified the proportionality of the intensity scattered by a \([\xi \xi 0]\) (\(\xi = 0.075\)) phonon to the sample thickness (between 1 and 10 mm) both in transmission and reflection geometry. This outcome still would not exclude the presence of a coherent "extinction" effect.

Let us recall that elastically deformed crystals provide Bragg scattered intensity proportionate to crystal thickness but being significantly less than that predicted by a kinematical formula.\(^8\)
Therefore in a next step we have compared intensities of both Bragg diffraction and phonon scattering from a perfect Si plate placed in a bending device. As displayed in Fig.1, upon bending the crystal with a radius of about 20 m, the intensity of the (335) Bragg reflection increased by nearly two orders of magnitude (close to the kinematical limit) while the intensity due to $[\xi\xi\xi]$ LA phonon remained unchanged. The combination of this outcome together with the proportionality between the intensity and the sample thickness provides a strong evidence for the validity of 1st Born (kinematic) approximation in neutron coherent inelastic scattering even by crystals of an extremely high quality.

![Graphs showing intensity vs. energy](image)

Fig.1 Intensities of a (335) Bragg reflection (a) and of a $[\xi\xi\xi]$ phonon line for a perfect (o) and a bent (●) crystal. The deformation increases the Bragg intensity from the dynamical to the kinematical limit while it has no effect on the inelastic scattering which is always kinematic.

In the final stage intensities due to the [00\xi] and $[\xi\xi\xi]$ phonons were measured in four different Brillouin zones, (224), (333), (115) and (335), using $E=const.$ scans. The integrated intensities were determined by fitting Gaussian profiles to the observed peaks, in most cases they corresponded to 500-1000 counts. In a further step the structure factors (Fig.2) were extracted from the integrated intensities with the help of eq.(5). Each set of 8 structure factors observed at a given energy transfer between 3 and 10 THz was then fitted by a model corresponding to eq.(6). At energy transfers below 6 THz it proved
Fig. 2 The normalized inelastic structure factors \( f(\vec{Q})/f_0 \) for the \([\xi\xi\xi]\) LA phonons observed in four different Brillouin zones. The solid lines connect fitted values with phases given in Fig. 3.

Fig. 3 The phase of polarization vectors of \([\xi\xi\xi]\) phonons: present results (*) in comparison with those of Strauch et al.\(^5\) (o) and with the prediction of recent \textit{ab initio} calculations\(^9\) (solid line).
necessary to include a separate scale factor for the $[\xi \xi \xi]$ phonons being by up to 13% higher than that for the $[00\xi]$ branch. Taking into account this increase in intensity (most probably due to differences in scattering surface curvature) had, anyways, only negligible influence on the refined phases given in Fig.2. Their values at medium $\xi$ coincide with the previous results obtained on silicon$^5)$ as well as with the results of recent \textit{ab initio} calculations$^9)$ while their turn back to zero about $\xi=0.4$ seems to be somewhat smoother.

CONCLUDING REMARKS.

The present results demonstrate the feasibility of exploitation of the information contained in intensities of coherent inelastic scattering. Unlike analogous preceding experiments we were able to utilize all the intensity data as in the set of 64 observed structure factors Fig.2) only two values exhibited departures as big as 20% from those predicted by the ensemble average while the majority staid well within 5-10% - a situation which is not too different from that met in crystallography.

This progress had to be paid for by certain limitations in the strategy of the experiment: scattered intensities corresponding to the same phonons, or at least same energy transfers, in different Brillouin zones were compared making necessary a considerable redundancy of the data set. The E=const. scans, used exclusively, provided certainly better stability of the observed intensities with respect to instrumental effects (variation of effective fluxes and efficiencies with neutron energy) but their application is limited to sufficiently steep branches (LA) only. It remains a matter of further investigations whether more sophisticated data processing techniques would make the Q=const. scans applicable as well.

Acknowledgements.

This work was enabled by the JAERI's Foreign Researcher Inviting Programme which provided travel funds for one of the authors (J.K.). It is a pleasure to acknowledge the kind support of S.Funahashi (JAERI) and B.Dorner(Ill) through all stages of this project, fruitful discussions with M.Iizumi(JAERI) as well as expert technical assistance of N.Minakawa and Y.Shimojo during the experiments. The silicon samples were kindly donated by Dr.W.Zulehner from Wacker Chemitronic (FRG).
REFERENCES.

7) G.Dolling, V.F.sears, Nucl.Inst.Meth. 106 (1973) 419.
9) P.Pavone, D.Strauch, S.Baroni, (to be published).
SPINODAL DECOMPOSITION IN FLUID MIXTURES

Kyozi Kawasaki and Tsuyoshi Koga

Department of Physics, Faculty of Science
Kyushu University 33, Fukuoka 812, Japan

ABSTRACT

We study the late stage dynamics of spinodal decomposition in binary fluids by the computer simulation of the time-dependent Ginzburg-Landau equation. We obtain a temporally linear growth law of the characteristic length of domains in the late stage. This growth law has been observed in many real experiments of binary fluids and indicates that the domain growth proceeds by the flow caused by the surface tension of interfaces. We also find that the dynamical scaling law is satisfied in this hydrodynamic domain growth region. By comparing the scaling functions for fluids with that for the case without hydrodynamic effects, we find that the scaling functions for the two systems are different.

INTRODUCTION AND MODEL

The dynamics of ordering processes in quenched fluids has been receiving a great deal of attention. Since the hydrodynamic effects play an important role in spinodal decomposition in such fluids, it is necessary to take such effects into account in order to study the dynamics in these systems.

Here we consider binary fluids and assume that the fluid is incompressible. In order to describe the spinodal decomposition of binary fluids, we introduce a local order parameter \( S(r) \), e.g. the local concentration, and the transverse component of the local velocity \( v(r) \). When the relaxation of the local velocity is more rapid compared to that of the local order parameter, we can eliminate the local velocity by assuming that the local velocity instantaneously follows the changes in the local order parameter. As a result, we obtain the following time-dependent Ginzburg-Landau (TDGL) equation for binary fluids:

\[
\frac{\partial}{\partial t} S(r, t) = L \nabla^2 \mu(r) - \nabla S(r) \cdot \int T(r - r') \cdot \nabla' S(r') \mu(r') dr',
\]

where \( \mu(r) \equiv \delta H[S]/\delta S(r) \) is the chemical potential, \( H[S] \) the Ginzburg-Landau type free-energy functional, \( L \) the Onsager kinetic coefficient and \( T(r) \) the Oseen tensor given...
by

\[ T(r) = \frac{1}{8\pi\eta} \left( \frac{1}{|r|} + \frac{\mathbf{r}\mathbf{r}}{|r|^3} \right). \] (2)

Here \( \eta \) is the shear viscosity and \( \mathbf{1} \) is the unit tensor. The second term on the right-hand side of Eq.(1) can be regarded as the long-range hydrodynamic interaction between the order parameter fluctuations. We have ignored the thermal noise in Eq.(1) because we are interested in the dynamics in the very late stage of spinodal decomposition.

To integrate Eq.(1) numerically, we employ the cell-dynamic method.\(^6\) Since a great deal of computational resources is required to compute the integral in the second term in real space, we calculate this integral in Fourier space using Fast Fourier Transform. Details of the numerical method have been reported elsewhere.\(^7\),\(^8\) The system used is a three-dimensional cubic lattice of size \( 128^3 \) with periodic boundary conditions.

RESULTS

Growth Law

In order to study the dynamics of spinodal decomposition quantitatively, we calculate the normalized structure factor \( I_K(t) \) defined by

\[ I_K(t) = \langle S_K(t)S_{-K}(t) \rangle / \int dK \langle S_K(t)S_{-K}(t) \rangle, \] (3)

where \( S_K \) is the Fourier component of \( S(r) \). We also compute the pair-correlation function \( G(r,t) \):

\[ G(r,t) = \langle S(0,t)S(r,t) \rangle. \] (4)

The spherically averaged structure factor \( I_K(t) \) and pair correlation function \( G(r,t) \) are calculated from \( I_K(t) \) and \( G(r,t) \), respectively.

We use the first moment of \( I_K(t) \) denoted as \( k_1(t) \) as the characteristic wave number and also use as the characteristic length of domains the length \( R_0(t) \) which is defined as the value of \( r \) where \( G(r,t) \) first crosses zero.

Figure 1(a) shows the time dependence of \( k_1(t) \) and the negative slope in this figure gives the exponent \( z : k_1(t) \sim t^z \).

According to earlier theoretical studies,\(^2\),\(^3\) the domain growth in the late stage of spinodal decomposition in fluid systems is driven by the flow induced by the surface tension and, in this case, the normal component of the velocity of the interface \( v_n \) is given by

\[ v_n \sim \frac{\sigma}{\eta}, \] (5)

where \( \sigma \) is the surface tension. By assuming that at the late stage of spinodal decomposition there is one characteristic length scale \( \ell(t) \) associated with domains, we find \( \ell(t) \sim \sigma/\eta\ t \) from Eq.(5), which gives the exponent \( z = 1 \). Our results in Fig.1(a) shows that the value of \( z \) increases rapidly after about 100 time steps and becomes its expected
value 1 in the late time region after 400 time steps. This result is also confirmed for $R_0(t)$ as shown in Fig.1(b).

Dynamical Scaling Law

We study the scaling law for $I_k(t)$ in the hydrodynamic domain growth region where the exponent $z = 1$,

$$I_k(t) = k_1(t)^{-3}F(z).$$

Here $F(z)$ is the scaling function and $z = k/k_1(t)$ the scaled wave number. The scaling plots for $I_k(t)$ at $t = 400 - 600$ time steps is presented in Fig.2.

This figure shows that the dynamical scaling law is satisfied in this time region. In this figure, we also find the following three features. (i) For large $z$, $F(z)$ approaches the form $F(z) \sim z^{-4}$, which corresponds to Porod's law.\(^9\) The deviation of $F(z)$ from Porod's law at large $z$ is due to the finite thickness of the interfaces. The effects of the interface thickness can be removed by the "hardening" transformation\(^10\) : $S(n) \rightarrow S_s\text{sgn}(S(n))$. The hardened scaling function is also presented in Fig.2(b). We can see that the hardened data clearly show Porod's law at $z \simeq 3 \sim 5$. (ii) For small $z \lesssim 1$, $F(z)$ is close to the form $F(z) \sim z^4$. (iii) In recent experiments on polymer blends, the "shoulder" is observed at $k \sim 3k_1;\(^11\) which can also be observed in Fig.2(b).
Fig. 2 Scaling plots of the normalized structure factor $I_k(t)$. The symbols $\circ$, $\triangle$, $\square$, $+$, and $\Diamond$ correspond to $t = 400, 450, 500, 550$ and $600$ time steps, respectively. In (b), the symbol $\times$ corresponds to the hardened data at $t = 600$ time step.

These features are consistent with the recent experimental data of polymer blends, in which the exponent $z \approx 1$ has been obtained and the hydrodynamic effects seem to be the dominant mechanism of the domain growth.

On the other hand, the features of $F(x)$ observed in Fig. 2(b) is similar to those for a system without hydrodynamic effects. For purposes of comparison, we performed the computer simulation using Eq.(1) without the second term on the right-hand side. We call this model "solid" here. A comparison of scaling functions for fluid and solid are presented in Fig.3. From this figure, we find that the peak height of the scaling function for fluid is lower than that for solid and the peak width of $F(x)$ for fluid is greater than that for solid.

Next we study the scaling law for the normalized pair correlation function $G_n(r, t) \equiv G(r, t)/G(0, t)$ which predicts

$$G_n(r, t) = \hat{G}_n(\tilde{r}),$$

(7)

where $\tilde{r} \equiv r/R_0(t)$. The scaling plots of $G_n(r, t)$ for fluid is presented in Fig.4. From this figure, we see that the scaling law for $G_n(r, t)$ seems to be well satisfied. Note that the real space scaling function $\hat{G}_n(\tilde{r})$ is slightly time-dependent, because the normalization factor $G(0, t)$ is increasing in time due to the decreasing interfacial area. To avoid this difficulty, we use the hardened data for $\hat{G}_n(\tilde{r})$ when we compare the scaling functions, since $G(0, t)$ for the hardened data is constant in time.

We compare the real space scaling functions for fluid and solid in Fig.5, where we
Fig. 3 Comparison of the scaling functions for fluid (○) and solid (+) obtained in the late stage.

Fig. 4 Scaling plots of the normalized pair correlation function $G_n(r)$ for fluid. Time steps are the same as those in Fig. 2.

Fig. 5 Comparison of the hardened scaling functions for fluid (○) and solid (+) in real space.

find the following features: (i) The amplitude of the oscillation of $\hat{G}_n(\tilde{r})$ about zero for fluid is smaller than that for solid. This corresponds to the fact that the peak width of $F(x)$ for fluid in Fourier space is greater than that for solid. (ii) The values of $\tilde{r}$ where $\hat{G}_n(\tilde{r})$ crosses zero after the first crossing are almost the same for both systems.
CONCLUSION

We presented the results of computer simulation runs of spinodal decomposition in binary fluid. We clearly observed the temporally linear domain growth law in the late stage. By comparing the scaling functions for fluid and solid, we found the definitive evidence of the difference in the scaling functions for the two systems.

ACKNOWLEDGMENTS

The work was supported by Grant-in-Aid for Scientific Research on Priority Areas "Computational Physics as a New Frontier in Condensed Matter Research", from the Ministry of Education, Science and Culture, Japan as well as by the Joint Program of the National Institute for Fusion Science.

REFERENCES

SMALL ANGLE NEUTRON SCATTERING STUDY ON A PHASE SEPARATION IN A 3-COMPONENT MICROEMULSION SYSTEM

Hideki SETO, Dietmar SCHWAHN, Kell MORTENSEN, Eiji YOKOI, Shigehiro KOMURA, Jun’ichi SUZUKI, Satoru FUNAHASHI and Yuji ITO

FIAS, Hiroshima University, Higashihiroshima 724, Japan

IFF, KFA Jülich, D-5170 Jülich, Federal Republic of Germany

RISØ National Laboratory, DK-4000 Roskilde, Denmark

Department of Physics, JAERI, Tokai, Ibaraki 319-11, Japan

ISSP, University of Tokyo, Roppongi, Tokyo 106, Japan

ABSTRACT

The mixture of three components, water, n-decane and AOT, is a well-known system that forms a "water-in-oil" microemulsion at room temperature and decomposes with increasing temperature, thereby being associated with a critical phenomenon. Experimental results in previous literature indicate that the phenomenon is interpreted to be that of the 3D-Ising, but we obtained the meanfield behavior of the susceptibility at "near-critical region" by a small angle neutron scattering. The observed spinodal and binodal points were well explained assuming the van der Waals free energy expression.

INTRODUCTION

An oil rich mixture of AOT (2-ethylhexylsulfosuccinate), water and n-decane is a well-known system which forms "water-in-oil" microemulsion, that is, water droplets coated with AOT film dispersed in n-decane, at room temperature. The droplet size is supposed to be constant when the temperature or concentration is varied, provided that the ratio of the amount of water to that of AOT is kept constant, and that the system remains to be mono-disperse. With increasing temperature, the system decomposes into two phases, droplet rich and poor domains. Below the decomposition temperature, a density fluctuation of the droplets occurs and grows stronger with increasing temperature. The density fluctuation determines the critical phenomena near the critical temperature $T_c$. An observations by small angle neutron scattering (SANS) or light scattering (LS) may reveal that the correlation length and the susceptibility (osmotic compressibility) of the fluctuations become infinite at $T_c$ according to
\( \xi = \xi_0 e^{-\nu} \) and \( \chi = \chi_\nu e^{-\gamma} \), where \( \nu = (T - T_c)/T \) is the normalized temperature and \( \gamma, \nu \) are the critical exponents. From these observed critical exponents, one can determine the universality class of the system such as meanfield theory (\( \gamma = 1.0, \nu = 0.5 \)) or 3 dimensional Ising model (\( \gamma = 1.24, \nu = 0.63 \)). Several authors\(^{2-6} \) have investigated this phenomenon with SANS or with LS. As summarized by Roux et al.,\(^5 \) the present trend of interpretation of the observed critical exponents is those of 3D-Ising. However, the critical exponents are somewhat different from the exact values of 3D-Ising, for example, \( \gamma = 1.30 \) and \( \nu = 0.76 \).\(^{2} \) (Honarat et al.\(^5 \))

It must be taken into account that the meanfield theory is plausible in a "near-critical region", where a fluctuation of an order parameter increases exponentially but is not large enough as compared with the order parameter itself.\(^7 \) Schwahn et al.\(^8 \) and Bates et al.\(^9 \) recently verified the meanfield behavior in a near-critical region and a crossover to the Ising behavior for polymer blend systems. In micellar systems, some experimental evidences supporting the meanfield behavior were obtained by some authors.\(^10 \)

From these points of view, we have examined the critical behavior by the small angle neutron scattering at RISØ National Laboratory for the 3 components microemulsion system, and showed the meanfield behavior for the critical exponent of the susceptibility at the near-critical region. At the same time, we have determined the binodal points and the spinodal points for 4 compositions. The observed phase diagram was explained by introducing a phenomenological Gibbs' free energy expression in a framework of the van der Waals theory with the generalized Flory-Huggins parameters. In order to confirm the result, further experiments for other concentrations were performed at the new SANS spectrometers at JRR-3M in JAERI. The meanfield behavior for the susceptibility was reproduced, but the critical concentration was not determined.\(^11 \)

**THEORETICAL**

In case of an ionic surfactant, charged ions depart from the surfactant layer and drift inside the droplet, resulting in a charge fluctuation in each droplet. Therefore an assumption of the van der Waals interaction between droplets is relevant.\(^12 \) Because the van der Waals model is equivalent to the meanfield approximation in describing critical phenomena, the model is suitable for the system which has the meanfield values of critical exponents. In this model, the Gibbs' free energy is known to be\(^13 \)

\[
F = N \psi(T) - N k_B T \ln \frac{N}{N - N^2 b} \frac{N^2 b}{V} a, \tag{1}
\]

where \( \psi(T) \) is the free energy per particle of ideal gas, \( N \) the number of particles, \( b \) the effective volume of each particle, and \( a \) an integrated potential energy of van der Waals force. By normalizing it in dimensionless form,

\[
f \equiv \frac{F}{(V / N^2) k_B T} = \phi \left( \ln \Omega \left( \frac{1}{\phi} \cdot b' \right) + c(T) \right) - \phi^2 \chi(\phi, T), \tag{2}
\]

with \( \phi \), the volume fraction of droplets which is the order parameter in this system, \( \Omega \equiv \phi V / N \), a volume assigned to each particle, and \( b' \equiv b / \Omega \), effective volume factor of each particle, where \( c(T) \) includes the \( \phi \)-independent terms and \( \chi(\phi, T) = a / \Omega^2 T \) is the Flory-Huggins

---

1. 
2. 
3. 
4. 
5. 
6. 
7. 
8. 
9. 
10. 
11. 
12. 
13.
parameter. For a lower critical solution temperature (LCST) case, this parameter should be written as

$$\chi(\phi, T) = \frac{\chi_h(\phi)}{T} - \chi_\sigma(\phi),$$  

(3)

where $\chi_h(\phi)$ is an enthalpic part and $\chi_\sigma(\phi)$ is an entropic part. The forward scattering is related with the Gibbs' free energy by the thermodynamical relationship

$$S(0)^{-1} = \frac{\partial^2 f}{\partial \phi^2} = 2(\Gamma_h - \Gamma),$$  

(4)

with

$$\Gamma_h(\phi) = \frac{1}{2\phi(1-\phi)b^2},$$  

(5)

$$\Gamma(\phi, T) = \frac{\Gamma_h(\phi)}{T} - \Gamma_\sigma(\phi),$$  

(6)

where $\Gamma_h$ and $\Gamma_\sigma$ are called the generalized Flory-Huggins parameters. For a system with LCST, both the parameters $\Gamma_h$ and $\Gamma_\sigma$ must be negative. From these equations, the temperature dependence of $S(0)$ yields

$$S(0)^{-1} = 2\Gamma_h\left(\frac{1}{T_s} - \frac{1}{T}\right),$$  

(7)

where the spinodal temperature $T_s$ is given by

$$T_s = \Gamma_h / (\Gamma_\sigma + \Gamma_h).$$  

(8)

Using these expressions, spinodal points $T_s$ and the generalized Flory-Huggins parameters $\Gamma_h$ and $\Gamma_\sigma$ can be determined experimentally.

**EXPERIMENTAL**

All the samples were prepared at the same water-to-AOT ratio as the 3 / 5 / 95 composition microemulsion, which is the mixture of 3g of AOT, 5ml of water and 95ml of n-decane.2) The volume fraction of both the surfactant and water mixture against the n-decane, $\phi$, is the order parameter, because it is directly proportional to the droplet density in the whole system (see Fig. 1). The 99 % (for RISO experiments) and 98 % (for JAERI experiments) AOT purchased from Aldrich Chemical Company, 99.8% heavy water supplied
by Merck and the 99% n-decane by Aldrich Chemical Company were used without any treatments. The mixtures were sealed in a niobium cell with 1 mm thick quartz-window.

In the first experiments, SANS spectrometer in RISØ National Laboratory was used. The incident neutron beam taken from reactor was monochromatized to be 15 Å and 4 Å by a mechanical velocity selector with a wavelength resolution of 18 %. A multi-wire 2 dimensional proportional counter placed at 6 m apart from the sample position was used. The observed momentum transfer ranges over $2.3 \times 10^{-3} \leq Q \leq 1.7 \times 10^{-2} \text{[Å}^{-1}]$ for 15 Å and $1.7 \times 10^{-2} \leq Q \leq 6.6 \times 10^{-2} \text{[Å}^{-1}]$ for 4 Å incident neutrons. The sample cell was placed in a vacuum chamber contained in an electric furnace controlled within 0.1 K by a computer.

The second SANS measurements were carried out with the SANS (C3-2) and SANS-U (C1-3) spectrometers at JRR-3M in JAERI, Tokai. The 6.4 Å and 7 Å incident neutron beams, taken from the cold neutron source and monochromatized by mechanical velocity selectors were used, respectively. Observed momentum transfer ranges over $5.5 \times 10^{-3} \leq Q \leq 1.4 \times 10^{-2} \text{[Å}^{-1}]$ for SANS and $1.7 \times 10^{-2} \leq Q \leq 3.3 \times 10^{-2} \text{[Å}^{-1}]$ for SANS-U, and the wavelength resolutions were 13 % and 10%, respectively. The multi-wire 2-dimensional position sensitive proportional counters placed at 10 m and 12 m apart from the sample position were used. The raw data were radially integrated and calibrated into differential cross sections versus wave-number using the incoherent scattering from a cell filled with light water as a standard sample for the cross section. The sample cell was placed in an electric furnace controlled within 0.005 K by two platinum resister temperature sensors and a PID-type control program running at a personal computer.

**EXPERIMENTAL RESULTS AND ANALYSIS**

Following the discussions in **INTRODUCTION**, the droplet shape is assumed to be spherical. Inset of Fig. 2 shows the example of Guinier plot for $\phi = 0.1031$ obtained at RISØ. One finds a wide range of the straight line corresponding to the Guinier formula, thus the system is supposed to be mono-disperse. From the slope of the fitted line, a Guinier radius $R_G$ was derived to be 53.4 Å.

As concerns the temperature dependence of the droplet radius, we found that the droplet radius tends to decrease with increasing temperature with a rate of -0.33 [Å/K], in contrast to the belief so far that the radius was kept constant with a temperature variation (see Fig. 2). Thus we used the temperature dependent form factor using both the Guinier radius at certain temperature and the observed rate of changing.

---

*Fig. 2* Temperature variation of the Guinier radius for $\phi = 0.1031$ is shown. The solid line indicates the fitted straight line. The inset figure is an example of the scattering profile in the Guinier plot.
Figure 3 displays a typical temperature variations of the structure factor in the Zimm plot at low-$Q$ region, below about $Q = 8 \times 10^{-3}$ [Å$^{-1}$], obtained at RISØ. If $S(Q)$ follows the Ornstein-Zernike formula, the profile must be a straight line with a slope $S_0^{-1} \xi^2$ and an intercept on the ordinate at $S_0^{-1}$, where $S_0$ is the forward scattering and $\xi$ the correlation length. From the fitted straight line, the temperature dependence of the forward scattering $S_0$ was obtained as are presented in Fig. 4. The inverse forward scattering is found to be proportional to $T$ within 10 K from the transition point. This means the critical exponent $\gamma$ for the susceptibility $\chi$ is about 1.0, which is the meanfield value, and at the same time, the spinodal point can be obtained from the intercept of these fitted straight lines on the abscissa, and the binodal point is also obtained from the 'kink', where $S_0$ stops to diverge. For other concentrations, $\phi = 0.0744$, 0.0950 and 0.1278, we obtained the similar results. In Fig. 5, similar results obtained at JAERI are shown. For several different concentrations, the meanfield behavior of the susceptibility at near-critical region was confirmed.

The temperature variation of the susceptibility obtained at RISØ was compared with eqs. (4) and (5). From the slope of the fitted straight line and the extrapolation onto the abscissa, $T_B$ and $T_s$ were given. The composition dependence of $T_B$ can be expressed by a 2nd order polynomial of the order parameter $\phi$, as

$$I_B(\phi) = 1322 - 72920 \phi + 349900 \phi^2 \text{[K]}, \quad (9)$$

(see Fig. 6(a)). We used $b' = 4$ because this value is typical from the textbook. Note that the value of $b'$ was not effective to the final results. $T_s$ is calculated from eq. (5), and $I_B$ is calculated using the experimental value of $T_t$ from eq. (8). The parameter $I_B$ also seems to be expressed by the 2nd order polynomial as

$$I_B(\phi) = -18.63 - 7.840 \phi - 242.4 \phi^2, \quad (10)$$

(see Fig. 6(b)). Substituting eqs. (9) and (10)

![Fig. 3](image3.png)  
**Fig. 3** Temperature variation of the scattering profiles for $\phi = 0.1031$ at near-critical region in Zimm representation. The solid lines indicate the fitted straight lines to the Ornstein-Zernike formula. The open circles are the data taken at $\Delta T = 7.69$ K which is the difference from the spinodal temperature, the full circles at $\Delta T = 4.18$ K, the open squares at $\Delta T = 2.44$ K, and the full squares at $\Delta T = 0.81$ K.

![Fig. 4](image4.png)  
**Fig. 4** The temperature dependence of the observed forward scattering (susceptibility) for $\phi = 0.1031$ is presented. The vertical axis indicates the inverse forward scattering and the horizontal axis the inverse of absolute temperature.
Fig. 5 Temperature dependence of the susceptibility for various values of $\phi$ observed at JAERI. The meanfield behavior was confirmed and both spinodal and binodal points were obtained.
to eq. (5), we obtain the $\phi$-dependence of the spinodal temperature expressed in units of K as

$$T_s = \frac{1322 - 72920 \phi + 349900 \phi^2}{1 / (2 \phi (1 - \phi b)^2) - 18.63 - 7.840 \phi - 242.4 \phi^2}$$  \hspace{1cm} (11)

which is indicated by the dashed line in Fig. 6(c) and explains well the observed spinodal points.

From the definition of $\Gamma$ (eq. (4)), the free energy can be expressed as a function of the order parameter $\phi$. The binodal points are usually given by calculating the points of contact of a common tangent line to the free energy curve with double minimum for each temperature. The solid line appearing in Fig. 6(c), represents the calculated binodal line in this way.

In Fig. 7, the detailed phase diagram between $\phi = 0.092$ and 0.099 obtained at JAERI is shown. The spinodal line seems to explain the observed points well, but the binodal line has a little discrepancy with the observed points, and we could not find the critical point.

---

**Fig. 6** The observed Flory-Huggins parameters (a) $\Gamma_h$ and (b) $\Gamma_c$, and the phase diagram are shown. The open circles in (a) and (b) are the observed points and the solid lines the fitted 2nd order polynomials. The open circles in (c) are the spinodal points, squares the binodal points, the dashed line the calculated spinodal line, and the solid line the binodal line, respectively.

**Fig. 7** The phase diagram obtained at JAERI. The open circles and the hatched circles also indicate the observed spinodal points and binodal points, respectively, and the dashed and the solid lines are the calculated spinodal and binodal lines.
DISCUSSION AND CONCLUSION

The most important result of this experiment is the finding of meanfield behavior of the system at the "near-critical region". In this region, the correlation length is not very large. Approaching closer to the critical point, the correlation length grows more. Then the meanfield approximation must break down and another behavior, e. g., 3D-Ising, might appear. We suppose that the previous results in literature which indicated somewhat different values from the exact Ising values, might be due to such a crossover. Within the results obtained at JAERI, the meanfield behavior was confirmed, but the crossover was not found. The reason of the absence of the critical concentration is a future problem.

To summarize, in order to explain the critical behavior, the van der Waals model with the Flory-Huggins interaction parameter is introduced. Comparing the experimental results with the free energy expression, the phase diagram in terms of temperature versus droplet density is calculated. A reasonable result is obtained in the region of dilute water composition range where the structure is thought to be the dispersion of the water-in-oil droplets with the same radius.

ACKNOWLEDGMENTS

This work is supported by the Nissan Science Foundation and a Grant-in-Aid for Scientific Research (No. 04740200) from the Japanese Ministry of Education.

REFERENCES

11) Details of these results were submitted to J. Chem. Phys. (1993).
NEUTRON DIFFRACTION FROM LEAD GERMANATE GLASSES

Norimasa UMESAKI, Thierry M. BRUNIER, Adrain C. WRIGHT, Alex C. HANNON and Rojer N. SCINCLAIR

Government Industrial Research Institute, Osaka 1-8-31, Midorigaoka, Ikeda, Osaka 563, Japan

J. J. Thomson Physical Laboratory, Reading University Whiteknights, Reading RG6 2AF, U.K.

ISIS Science Division, Rutherford Appleton Laboratory Chilton, Didcot, Oxon OX11 0QX, U.K.

Industrial Technology, Harwell Laboratory Chilton, Didcot, Oxon OX11 0RA, U.K.

ABSTRACT

High resolution neutron diffraction data have been collected on the PbO-GeO₂ glasses and on GeO₂ for comparison. These neutron data have revealed the existence of 6-fold coordinated germanium (GeO₆ octahedra) by virtue of the shift in the first peak in the obtained total correlation function T(r) and increase in the coordination. The neutron results also indicate that PbO exits as PbO₄ pyramids, as found in the orthorhombic form of PbO crystal, in the studied PbO-GeO₂ glasses.

INTRODUCTION

Much recent research of fiber optic materials has involved the development of ultra low loss, long wavelength optical waveguides, which can operate further in the infrared region than the 1.7μm limit of fused silica-based compositions. The potential of germania-based compositions for such devices has been demonstrated since these can operate at wavelengths greater than 3μm with losses as low as 0.01dB/km¹-⁴. In order to develop oxide glasses that will shift their infrared transmittance to long wavelengths, large cations with low field strength can be added. Germanate glasses containing lead oxide are most suitable for such optical waveguide materials⁵. Although glass formation has been reported in PbO-GeO₂ system⁶-⁹, very little is known about the structure and properties of such glasses. Topping et al.⁷ indicated from the analysis of the molar volume data that the coordination number of some Ge⁴⁺ ions in the binary glasses changed from 4 to 6 when PbO was added. Recently, Canale et al.⁵ discussed the structure and properties of glasses in the binary PbO-GeO₂ and Bi₂O₃ systems on the basis of interpretation of their vibrational spectra and molar volume data. Umesaki¹⁰ reported the radial distribution function (r.d.f.) of glassy and molten PbGeO₃ obtained from the X-ray diffraction data, and suggested the structural model based on PbO₄ pyramid and network forming GeO₄ tetrahedra.
In the present work, in order to clarify the atomic scale structure of glasses in the binary PbO-GeO₂ system, we performed high resolution neutron diffraction measurements on three lead germanate glasses with the compositions PbO·4GeO₂, PbO·2GeO₂ and 2PbO·3GeO₂. The obtained neutron structural data were compared with that of vitreous GeO₂ whose structure has been studied previously by Desa et al.¹¹).

EXPERIMENTAL PROCEDURES

Preparation of Binary PbO-GeO₂ Glass

Three glass samples in the binary PbO-GeO₂ system were prepared for measurement by quenching from the melt. The glass compositions, their measured densities and the glass dimensions are listed in Table 1. The lead monoxide used was BHC Chemical Limited AnalR

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>Temperature (°C)</th>
<th>Melting Time (hours)</th>
<th>Rod diameter (cm)</th>
<th>Density (c.u.Å⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeO₂¹¹)</td>
<td>1200, 1400</td>
<td>6, 4</td>
<td>5.261</td>
<td>0.0209905</td>
</tr>
<tr>
<td>PbO·4GeO₂</td>
<td>1350</td>
<td>4</td>
<td>5.291</td>
<td>0.0048194</td>
</tr>
<tr>
<td>PbO·2GeO₂</td>
<td>1140, 1040</td>
<td>4, 1</td>
<td>5.530</td>
<td>0.0078622</td>
</tr>
<tr>
<td>2PbO·3GeO₂</td>
<td>1120</td>
<td>3</td>
<td>5.521</td>
<td>0.0047144</td>
</tr>
</tbody>
</table>

PbO quoted 99% purity. The germanium oxide used was Koch-Light GeO₂ quoted at 99.999% purity. Appropriate proportions of PbO and GeO₂ powders were ground in propan-2-ol to aid homogeneous mixing using an agent pestle and mortar. The mixture was put in a platinum crucible and melted. The alcohol evaporated and the resulting melt was clear and appeared to be homogeneously mixed. The PbO-GeO₂ melts were quenched by pouring into 5mm internal diameter steel chill. This chill was warmed to approximately 150°C and casting surfaces were highly polished. This was done to reduce the internal and surface stress in the glass rod. The rod was quickly removed and allowed to cool inside a split pyr muffle.

Neutron Diffraction

1. Theory

The quantity measured in a neutron diffraction experiment is the differential cross-section

\[
\frac{d\sigma}{dQ} = T^s(Q) + i(Q)
\]

where Q is the momentum transfer, \( T^s(Q) \) is the self scattering term and \( i(Q) \) is the distinct scattering term. The self scattering, which can be calculated within an approximation, is subtracted from the data to give the distinct scattering. Structural information may then be obtained by using a Fourier transform of the experimental interference function \( Q^s i(Q) \) to obtain the total correlation function

\[
T(r) = T^s(r) + \sum_{Q=0}^{\infty} T^s(Q)M(Q)\sin(Qr)QdQ
\]
where \( T^0(r) = 4\pi g^0\left(\sum c_i \bar{c}_i \right)^2 \) is the average density contribution, and \( M(Q) \) is a modification function used to take into account the maximum experimentally attainable value of \( Q \).

2. Experimental

Fig. 1 The CURRAN diffractometer at the Harwell A.E.R.E.

Fig. 2 The LAD diffractometer at the Rutherford Appleton Laboratory.
The neutron experiments employed the same combination of the DIDO CURRAN at Harwell A.E.R.E (see Fig. 1) and the Liquid and Amorphous material Diffractometer (LAD) on 800MeV proton synchrotron spallation pulsed source ISIS at the Rutherford Appleton Laboratory (see Fig. 2). The CURRAN is a conventional twin axis diffractometer using a monochromatic beam of thermal neutrons, and the CURRAN data are usually more reliable in the low Q region. The LAD diffractometer uses the time-of-flight method, thus enabling very high Q-values to be achieved.

The CURRAN scattering data were obtained for the three glass samples, PbO·4GeO₂, PbO·2GeO₂ and 2PbO·3GeO₂, at an incident wavelength of 1.372Å (0.13≤Q≤0.739Å⁻¹). A vanadium standard (4.77±0.22mm diameter rod) and the empty sample position run were also done to perform the normalization and background correction. The neutron scattering lengths, b, for Ge, O and Pb were taken to be 0.81858×10⁻¹⁴m, 0.5804×10⁻¹⁴m and 0.94003×10⁻¹⁴m respectively. The obtained intensity data were normalized to the vanadium run and re-normalized using the Krogh-Moe-Norman technique. A cubic spline function was fitted to the normalized intensity data and the first diffraction peak was plotted out and extrapolated to Q=0Å⁻¹. The experimental interference function Q^2I(Q), which represents the diffraction properties of a sample in reciprocal space, was obtained from these smoothed intensity data.

The LAD experiment involved collecting data from the same three glass samples as used in the CURRAN experiments. In addition, data were collected on vitreous GeO₂. Data on each sample were collected as well as on a 6mm vanadium rod and an empty sample position. The sample: vanadium: background monitor ratio was set at 10: 10: 1. The background spectrum was subtracted from the sample and vanadium spectra and time of flight scale was converted to Q. The Q conversion was performed using the LAD analysis routines written at ISIS and the initial delay is constant, not a function of wavelength. Each vanadium spectrum from all the counters was fitted with a cubic spline function to extract the first derivative of the incident spectrum. The Placzek correction was applied to the vanadium and the new spectrum and first derivative were calculated by fitting a cubic spline again. The spectrum and derivative were used to normalize the sample spectra and perform the Placzek correction. The composition unit ratios were adjusted so that the corrected diffraction patterns for each counter oscillated evenly about the calculated self scattering. To use the superior count statistics of the 150° counters, a polynomial was fitted to I(Q) to emulate the self scattering. The composition unit ratios were adjusted by no more than 5%.

The twin axis data from CURRAN were plotted on a large scale with each counter of the time-of-flight LAD data to check the normalization of the LAD data and to obtain the regions of

Fig. 3 Interference functions Q²I(Q) for CURRAN and LAD counters on spline fit PbO·4GeO₂ glass.
best reliability for each counter. The low angle counters (5°, 10°) were excellent agreement with the CURRAN data. The high Q data were taken from the higher angle counters where the data appeared to be most reliable. The combined CURRAN and LAD $Q^*(Q)$ curves of the PbO·4GeO$_2$ glass are shown in Fig. 3. Fig 4 indicates the resulting $Q^*(Q)$ curve. As shown in this figure, oscillation in the PbO·4GeO$_2$ glass extended to 50Å$^{-1}$.

![Graph](image)

Fig. 4  Interference function $Q^*(Q)$ on spline fit PbO·4GeO$_2$ glass.

**RESULTS AND DISCUSSION**

The total correlation functions $T(r)$ were calculated for each of the PbO-GeO$_2$ glasses from the obtained $Q^*(Q)$ curves and are illustrated in Fig. 5. On addition of PbO, several interesting features are apparent. The wavelengths of the high Q oscillations in $Q^*(Q)$ curve tend to decrease with increasing PbO content as does the magnitude of these oscillations. This implies a peak shift in the first peak of $T(r)$ curve along with a decrease in its intensity as shown in Fig. 5. Other features that are altered are a peak at 2.3Å which increases with increasing PbO content, a small shift in the peak at 2.8Å a decreasing of the 3.3Å and 4.4Å peaks.

The peak at 2.3Å can be identified as the first Pb-O distance from corresponding distances in the PbO crystal structures (yellow PbO$^{12}$) implies Pb-O bond length = 2.2-2.4Å, and red PbO$^{13}$ implies Pb-O bond length = 2.34Å). The O-O peak at 2.8Å tends to shift slightly to higher r. This could be due to either the formation of GeO$_6$ octahedra or the O-O distance in the PbO$_4$ tetrahedra. In order to look at the structural feature in the obtained $T(r)$ curves in more detail, we may consider the difference function i.e. PbO-GeO$_2$ T(r) minus GeO$_2$ T(r) as shown in Fig. 6. These correction functions have been normalized so that each composition unit contains one GeO$_2$ unit. The most striking feature in these curves is the growth of a sharp contribution on the falling edge of the first Ge-O peak. This peak is positioned at 1.9Å which indicates a structure related to the rutile form of germania crystal. Rutile GeO$_2$ is composed of GeO$_6$ octahedra as opposed to GeO$_4$ tetrahedra as is found in the pure vitreous GeO$_2$. The Ge-O distance in this form is 1.872Å to 1.902Å. This peak grows with increasing PbO.

Peak fits were performed for the measured PbO-GeO$_2$ glasses and the parameters for these fits are given in Table 2. It can be seen that the Ge-O coordination number increases with increasing PbO which again indicates the presence of a more highly coordinated structural unit (GeO$_6$ octahedra). The value of the coordination number for the highest lead content glass
Fig. 5 Total correlation functions $T(r)$ for (A) GeO$_2$, (B) PbO·4GeO$_2$, (C)PbO·2GeO$_2$ and 2PbO·3GeO$_2$ glasses.

<table>
<thead>
<tr>
<th>Table 2 Peak fit parameters for PbO-GeO$_2$ glasses.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peak</strong></td>
</tr>
<tr>
<td>GeO$<em>2$ glass ($Q</em>{max}$=58Å$^{-1}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>GeO$<em>2$ glass ($Q</em>{max}$=42Å$^{-1}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PbO·4GeO$<em>2$ glass ($Q</em>{max}$=42Å$^{-1}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>PbO·2GeO$<em>2$ glass ($Q</em>{max}$=42Å$^{-1}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>2PbO·3GeO$<em>2$ glass ($Q</em>{max}$=42Å$^{-1}$)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Ge-O(4): four-fold coordinated Ge; Ge-O(6): six-fold coordinated Ge

(Coordination numbers $n_{jk}$ for Ge-O(6) give the contribution to the remaining area under the peak on the same scaling as Ge-O(4) so both sum to give the total coordination numbers.)

2PbO·3GeO$_2$ was 4.77 which implies that the ratio of six-fold coordinated Ge to four-fold coordinated Ge is approximately 1:3. This agrees with the estimated ratio in Na$_2$O-GeO$_2$ glasses.
by X-ray diffraction at the minimum in the germanate anomaly (1:3). Thus the fact that the anomaly is stronger in alkali germanate glasses is probably due to the network formation of the PbO reducing the overall packing efficiency.

It is difficult to say exactly in what form the PbO exists in the germanate glasses but some indication is given by comparison with its crystal polymorphs. Lead oxide exists in two crystal forms; red lead oxide Pb$_3$O$_4$ exists in bimolecular tetragonal units and yellow lead oxide PbO is orthorhombic. The values for the Pb-O distance are 2.33Å for tetragonal structure and 2.21Å to 2.42Å in the orthorhombic structure. Close inspection of the T(r) difference functions shows that the Pb-O peak is positioned at 2.33Å but its broadness indicates that the orthorhombic structure cannot be ruled out. The Pb-Pb distances found in the crystal polymorphs are 3.70-3.90Å in the tetragonal structure and 3.47-3.63Å in the orthorhombic structure. As shown in Fig.6, inspection of the difference functions shows a peak positioned at 3.55Å increasing in intensity with increasing PbO content which would suggest that this feature is due to the Pb-Pb correlations. The range defined by tetragonal PbO covers a minimum in the (PbO-4GeO$_2$-GeO$_2$) function and it is therefore very unlikely that this structural unit is occurring in the PbO-GeO$_2$ glasses. The peak maximum is close to the center of the range covered by the orthorhombic PbO Pb-Pb distance, and therefore it is reasonable to conclude that the PbO could exist as it does in orthorhombic PbO i.e. as pyramids of PbO$_4^-$ with all oxygens on one side of the Pb atom, one pair spaced at 2.21Å from the Pb atom and the other at 2.42Å. The coordination number for Pb-O correlation in the PbO-GeO$_2$ glasses is approximately 6. This is the value expected for the orthorhombic PbO (as opposed to 3 in tetragonal Pb$_3$O$_4$) which would agree with the previous points.

**REFERENCES**

PHASE FORMATION OF
PHYSICALLY ASSOCIATING POLYMER BLENDS

Fumihiko Tanaka

Department of Physics, Faculty of General Education
Tokyo University of Agriculture and Technology
Fuchu-shi, Tokyo 183, Japan

ABSTRACT

Polymers exhibit a variety of condensed phases when some of their segments are capable of forming weak bonds which can be created and destroyed by thermal motion. Transition from one phase to another caused by such "segment association" is reversible by the change of the temperature and the concentration, so that it is called "reversible phase transition". What types of reversible phase formation are possible for a given associative interaction? What is the most fundamental laws which govern the competition between molecular association and phase separation? This paper surveys, as typical examples of reversible phases, macroscopic phase separation, microphase formation, solvation, gelation, etc. from the unified point of view, and explores the possibility of new condensed phases caused by their mutual interference.

INTRODUCTION

In polymer blends or solutions, polymer chains often carry reactive groups capable of forming reversible interchain bonds. A description in terms of van der Waals type contact energy — or $\chi$-parameter in lattice theoretical terminology — is therefore insufficent in such associating polymers. These interactions include hydrogen bonding, ionic association, stereocomplex formation, cross-linking by the crystalline segments, solvent complexation, etc.[1]-[3]. Because the binding energy is of the order of thermal energy, bonds are created and destroyed by the thermal motion of the chains. Extensive polydispersity inherent in such associating solutions is thermally controlled. It is clear that consideration of interpolymer cross-linking interaction superimposed on the familiar description of statistical chains can lead to the application of the polymer science in numerous systems of practical importance. The purpose of present paper is to introduce a thermodynamic theory which describes formation of new phases brought by association [4]. We attempt to derive phase diagrams, paying special attention on the appearance of higher order multicritical phenomena caused by the interplay of the two competitive tendencies: molecular association and phase demixing. Results of the theoretical phase diagrams are compared with the experimental data presently available.

THERMODYNAMICS OF ASSOCIATING POLYMERS

Consider a binary mixture of linear polymers A and B. The number of statistical units on a chain is assumed to be $n_A$ for an A chain and $n_B$ for a B chain. We also assume that each chain carries a fixed number of reactive groups capable of forming bonds. In a thermal equilibrium, associative forces among the groups form intermolecular clusters with a wide spectrum of the aggregation number.
In what follows, we develop a lattice theoretical description of binary polymer mixtures by deviding the total volume $V$ of the system into small cells of the size $a$ [4]. We have total number $\Omega = V/a^3$ of the microscopic cells. We first specify the part of the system containing only the finite-size clusters, which will be referred to sol. The total volume fraction of A-chains in the sol is given by $\phi_A^S = n_A \sum_{l,m} \nu_{l,m}$, where $\nu_{l,m}$ is the number of clusters consisting of $l$ A-chains and $m$ B-chains (specified by the symbol $(l,m)$), and similarly $\phi_B^S = n_B \sum_{m} m \nu_{l,m}$ for B-chains. Contribution from the macronetwork is not included in the sum. The total volume fraction of the sol in the system is given by $\phi^S = \phi_A^S + \phi_B^S$. This should be equal to unity for nongelling systems or pre-gel regime, but becomes smaller than unity as soon as an infinite network (referred to as gel) appears (postgel regime). In the postgel regime we have the relations $\phi_i^S + \phi_i^G = \phi_i$ for $i = A, B$, where $\phi_i$ is the volume fraction of the species i, which is experimentally controlled. Since we have an identity $\phi_A + \phi_B = 1$, we can take $\phi_A$ as an independent variable and write it simply as $\phi$. The volume fraction of B is then given by $\phi_B = 1 - \phi$.

In order to study the thermodynamic properties, we start from the reference state in which unconnected A-chains and B-chains are prepared separately. We first consider the free energy change $\Delta F_{rea}$ to bring the system to a fictitious intermediate state in which the chains are connected in such away that the cluster distribution is exactly the same as the real one. It is given by

$$\beta \Delta F_{rea}/\Omega = \sum_{l,m} \Delta_{l,m} \nu_{l,m} + \delta_A \mu_A^G + \delta_B \mu_B^G,$$

where $\beta = 1/k_BT$ is the inverse temperature, and $\Delta_{l,m}$ the change in the internal free energy produced in the process in which a single $(l,m)$ cluster is formed from $l$ A-chains and $m$ B-chains. Similarly, $\delta_i$ $(i = A, B)$ are the free energy change produced when an isolated chain of the species $i$ becomes a part of the gel network. Let $\mu_{l,m}$ be the internal free energy of a $(l,m)$ cluster. The free energy difference $\Delta_{l,m}$ is then given by $\Delta_{l,m} = \mu_{l,m} - \mu_{0,0}$. Similarly we have $\delta_A = \mu_A^G - \mu_{0,0}^G$, and $\delta_B = \mu_B^G - \mu_{0,0}^G$. Under a constant pressure, $\mu_{l,m}$ is equivalent to the internal free energy due to the combination, configuration and the bond formation of the constitutional chains.

In the second step, we mix these clusters to form a real mixture. According to the lattice theory [5] of polydisperse polymer mixtures, the mixing free energy $\Delta F_{mix}$ in this process is given by

$$\beta \Delta F_{mix}/\Omega = \sum_{l,m} \nu_{l,m} \ln \phi_{l,m} + \chi \phi_A \phi_B,$$

where $\phi \equiv (n_A + n_B m) \nu_{l,m}$ is the volume fraction of $(l,m)$-clusters, $\chi$ the Flory $\chi$-parameter which specifies the strength of the van der Waals type contact interaction between the monomers of different species. $\chi$-parameter varies with the temperature. The total free energy from which our theory starts is given by the sum of the above two parts:

$$\Delta F = \Delta F_{rea} + \Delta F_{mix}.$$

By differentiation with respect to the number of molecules or clusters, we find the chemical potentials for the clusters.
Pregel Regime Having obtained the chemical potentials, we now impose the multiple equilibrium conditions to ensure the equilibrium distribution of the cluster. These are

$$\Delta \mu_{l,m} = l\Delta \mu_{1,0} + m\Delta \mu_{0,1}$$  \hspace{1cm} (4)

for all possible combinations of the integers \((l, m)\). Upon substitution of the chemical potentials, we find the volume fractions of the clusters to be given by \(\phi_{l,m} = K_{l,m}x^l y^m\), where we have written as \(x\) and \(y\) for simplicity for the unimer concentrations \(\phi_{1,0}\) and \(\phi_{0,1}\). The new constant \(K_{l,m}\) (called association constant) is defined by \(K_{l,m} = \exp(l + m - 1 - \Delta l_m)\), which depends only on the temperature through \(\Delta l_m\). The total volume fraction \(\phi^S\) is found by taking the infinite sum:

$$\phi^S(x, y) = \sum_{l,m} K_{l,m} x^l y^m.$$  \hspace{1cm} (5)

The total number of clusters \(\nu^S(x, y)\) is similarly found.

In order to study the thermodynamic properties, we must express the unimer concentration as a function of the total composition \(\phi\), which is controllable in the experiments. In the pregel regime this can be done by solving the coupled relations \(n_A x (\partial \nu^S / \partial x) = \phi\), and \(n_B x (\partial \nu^S / \partial y) = 1 - \phi\). Once we find \(x\) and \(y\) as functions of \(\phi\) (and the temperature \(T\)), we can express all physical quantities in terms of these two independent thermodynamic variables. The followings are important properties on which we will discuss in detail for specific systems:

(1) The osmotic pressure \(\pi\) of the A component is given by

$$\beta \pi / n_B a^3 = -\beta \Delta \mu_B / n_B = (1 + \log y) / n_B - \nu^S(x, y) + \chi \phi^2.$$  \hspace{1cm} (6)

In a polymer solution in which B component is a low molecular weight solvent \((n_B = 1)\), this definition reduces to the osmotic pressure in the conventional meaning.

(2) Two-phase equilibrium can be found by the balance of the chemical potential of each component:

$$\Delta \mu_A(\phi', T) = \Delta \mu_A(\phi'', T),$$  \hspace{1cm} (7a)

$$\Delta \mu_B(\phi', T) = \Delta \mu_B(\phi'', T),$$  \hspace{1cm} (7b)

where \(\phi'\) and \(\phi''\) are the composition of the dilute A phase and concentrated A phase respectively.

(3) The thermodynamic stability limit or spinodal can be found for a binary system by a single condition \((\partial \Delta \mu / \partial \phi)_T = 0\). Our result for \(\Delta \mu_A\) leads to the equation

$$\frac{\kappa_A(\phi)}{n_A \phi} + \frac{\kappa_B(\phi)}{n_B (1 - \phi)} - 2\chi = 0,$$  \hspace{1cm} (8)

where the new functions are defined by \(\kappa_A(\phi) = \phi \partial \log x / \partial \phi\) and \(\kappa_B(\phi) = -(1 - \phi) \partial \log y / \partial \phi\).

Sol-to-Gel Transition So far we have tacitly assumed that the infinite double summation in \(\phi^S\) (and hence for \(\nu^S\)) converges. For a solution capable of gelling, a borderline exists which separates the unit square on the \((x, y)\) plane into a convergent and divergent region of the infinite sum. Exactly on the boundary line, the sol composition
$\phi^S$ takes a finite value smaller than unity, but they diverge outside this line. Since the radius of convergence generally depends on the total composition, let us express the boundary by a parametric representation $(x^*(\phi), y^*(\phi))$ for $0 < \phi < 1$.

In the postgel regime, a chain participating in the gel network is in a chemical equilibrium with an isolated chain of the same species. This imposes additional conditions $x^* = \exp(\delta_A - 1)$ and $y^* = \exp(\delta_B - 1)$, if they are gelling. In the postgel regime $x$ and $y$ in the physical quantities must be replaced by these values. As a result we have, for example, a function $\kappa^*$ which is different from $\kappa$. The function $\kappa^*$ corresponding to a gelling component vanishes because it is proportional to the weight-average molecular weight.

**SCATTERING FUNCTIONS**

In order to find the condition for the microphase formation, we calculate the correlation function $S(q)$ of the concentration fluctuation—which is directly measurable in the X-ray or neutron scattering experiments—as a function of the wave vector, temperature and concentration. When it is divergently enhanced at a certain finite wave number $q$, it is the precursor of the instability against the fluctuations whose spatial variations have a characteristic length $q^{-1}$, thus leading to the formation of an ordered state with the periodicity $q^{-1}$. In the case of block copolymers, the domain size $q^{-1}$ is of the order of the radius of gyration of a single polymer chain, and hence called a microphase separation transition (MST). From the same viewpoint, we can also find the macroscopic stability limit—or spinodal condition (SP) discussed in the preceding section—from the condition $S(q = 0) = \infty$, which is equivalent to the divergence of the osmotic compressibility.

In order to obtain specific form of the correlation function $S(q)$, we now apply random phase approximation (RPA) [6]. RPA provides a classical treatment of concentration fluctuations for the incompressible mixtures of very large molecular-weight molecules. It assumes a self-consistent potential uniformly acting on all species of monomers to ensure the incompressibility condition. The detail of the RPA method, as applied to our polydisperse copolymer blend leads to

$$S(q) = 1 / \{ G(q) / W(q) - 2\chi \},$$

(9)

where $G(q) \equiv S_{AA}^0(q) + S_{BB}^0(q) + 2S_{AB}^0(q)$, and $W(q) \equiv S_{AA}^0 S_{BB}^0(q) - [S_{AB}^0(q)]^2$ are both related to the intrachain scattering functions (superscript $\circ$ shows the scattering intensity arising from a single cluster). For our associating blends, clusters are characterized by the set of two figures $(l, m)$, and so $S_{AB}^0$ for example, transforms into $S_{AB}^0(q) = \sum_{l,m} C_{lm}(q) \nu_{l,m}$, where $C_{lm}(q)$ is the monomer correlation functions of an isolated single cluster of the type $(l, m)$ [7]. The divergence condition for $S(q)$ leads to $G(q) / W(q) - 2\chi = 0$ within RPA. If this condition is satisfied for finite $q$, the system becomes unstable against the fluctuation in the concentration whose spatial dimensions are characterized by $q^{-1}$. If it is satisfied for $q = 0$ on the other hand, it is unstable against demixing into two coexistent macroscopic phases.

**SPECIFIC SYSTEMS**

For the numerical calculation of the phase diagrams we introduce the reduced temperature $\tau \equiv 1 - \Theta_0 / T$, where the unperturbed theta temperature $\Theta_0$ is the temperature which satisfies the equation $\chi(\Theta_0) = 1/2$, and hence the unrenormalized second virial coefficient of the osmotic pressure vanishes at this temperature. We then have $\chi(T) = 1/2 - \psi_1 \tau$. For the association constant, $\lambda(T) \equiv \exp(-\Delta f / k_B T)$ (here $\Delta f$ is the free energy of the single bond formation), we rewrite $\lambda(T) = \lambda_0 \exp\{\gamma(1 - \tau)\}$ with
the dimensionless binding energy $\gamma \equiv \Delta \varepsilon / k_B \Theta_0$ and the constant $\lambda_0 \equiv \exp(\Delta s / k_B)$, which is related to the entropy change $\Delta s$ in bonding.

**Dimerization** The first system we study is a mixture of A- and B chains in which diblock copolymers are formed by the end-to-end association (**hetero-dimerization**) [7]. A composite chain formed is a diblock copolymer A-B with a temporal junction in the middle. In an equilibrium, the system is made up of a mixture of diblock copolymers, and unreacted homopolymers of each species. It is apparently same as a mixture of chemically connected diblock copolymers dissolved in their homopolymers, but its phase behavior is in fact much richer, because the population of the block copolymers varies by the change in the temperature and the total concentration.

Fig.1 shows the phase diagram of a symmetric system where both chains have the same length. Solid lines show the spinodal, the broken lines MST. They meet at the two symmetric points (indicated by LP), at which the two conditions are simultaneously satisfied. They are examples of the *Lifshitz point*—the point where an order parameter with finite wave number starts to appear. The whole plane is divided into several regions, each characterized by the capital letters in it. The region with letter H has a homogeneously mixed fluid phase. The regions shown by M and M' exhibit microscopically ordered phases in which microdomains are regularly ordered. A region with two letters in the figure is a biphasic region (or *miscibility gap*) where two distinct phases indicated by the capital letters coexist. In the middle of the phase diagram we have an *eutectic point* (indicated by the letter e) where single microphase melt into the two coexistent homogeneously mixed fluids when the temperature is lowered. As the temperature is still lowered, we observe that the miscibility gap starts to split again at the point e' in the center of the concentration axis, and a new microphase (shown by M') becomes stabilized in between. The low-temperature microphase—which should be called a *reentrant microphase*—is stabilized simply because the population of block copolymers produced becomes so large in this low-temperature region that they homogenize the two demixed fluid phases into a single one. Prediction of the existence of such a new type of reentrant phase is one of the main conclusions obtained in our theory.

**Solvation** The next system we consider is a polymer solution in which solvent molecules attach onto the polymer chains by reversible bonds. We call this phenomenon *solvation* [8]. Our model predict that the solvation can lead to the peculiar types of phase separation with closed-loop and hour-glass type miscibility gaps.

Fig.2 show two possible phase diagrams. In this figure we have fixed the parameters as $\psi_1 = 1$, and $\gamma = 3.5$ (from the measured strength of the hydrogen bond in a solution) for a typical example. The number of the statistical unit on a polymer chain is varied from curve to curve. The number of attaching sites on a polymer chain is assumed to be proportional to the number of statistical units. The open circles show critical solution points. The solid curves show binodals, and the dashed curves spinodals. For $\lambda_0 = 0.002$, there are two miscibility gaps for small molecular weights: one miscibility dome and one closed loop above the dome (see $n = 10^2$ curve). The closed loop has one *upper critical solution temperature* (UCST) on the top and one *lower critical solution temperature* (LCST) on the bottom. The dome has an ordinary UCST. As the molecular weight is increased, the LCST and the UCST of the dome come closer and closer, and at certain value of n (several thousand in this figure) the two points merge into a higher order critical point (it is called *bicritical point*). For the molecular weights higher than this critical value, the two gaps merge into a single hour-glass shaped gap. For a slightly higher value of $\lambda_0$, however, it was found that the two gaps remain separated no matter how large the molecular weight may be. There are three theta temperatures under such condition to which each critical point approaches in the limit of high molecular weight. For a still larger value of $\lambda_0$, the closed loop gap does not appear, and we are left with
an ordinary miscibility dome. Since the parameter $\lambda_0$ is small if the entropy loss during the bond formation is large, there must be a strong orientational or configurational constraint in the local geometry for an hour-glass to appear.

Fig.3 shows the comparison [8] of the theoretical calculation with the observed phase diagram [9] for polyethylene oxide (PEO) in water. The number average molecular weight covers the range $2.17 \times 10^5 - 1.02 \times 10^6$. The solid curves show the calculated binodals. The number $n$ of the statistical unit on a chain is varied from curve to curve. The parameters used for the theoretical calculation are: $\psi = 1$, $\Theta_0 = 730 K$, $\gamma = 6$, and $\lambda_0 = 1.66 \times 10^{-5}$. Fitting is made mainly by adjusting the unknown parameter $\lambda_0$. The agreement is very good.

**Gelation** We next consider the case where polymers A form a gel in a solvent B. *Physical gelation* is the association in which clusters can grow to macroscopic networks. In the characterization of reversible gels, one has to clarify, for instance, the multiplicity $s$ of a junction—i.e., the number of chains connected by the junction—its lifetime $\tau$ and internal structure in addition to the average molecular weight $M$ between the adjacent junctions. The sol-to-gel transition point is defined by the point on the temperature-concentration plane at which the weight-average molecular weight of the clusters becomes infinite. In other words, gelation is the phenomenon that the connected part in the system grows macroscopically large. This condition is described by the divergence of the weight-average $< l >_w = \sum l K_{i,0} \phi_{1,0}^l / \sum K_{i,0} \phi_{1,0}^l$ of the association number of A chains.

**Pairwise Association** In the case where primary polymer chains are cross-linked by pairwise bonding ($s = 2$) among the functional groups attached on the chains, detailed study [10],[11] of the singularity in the power series in $< l >_w$ on the basis of tree statistics [12] shows the sol-to-gel transition is actually the phase transition of second order. This transition line intersects with the binodal. Fig.4(a)~(c) are the phase diagrams [11]. Solid lines show binodals (outer lines) and spinodals (inner lines), while the broken lines show the gelation transition. Three figures correspond to different three values of $\lambda_0$. We can see the change in competition between the two phase transitions depending upon the strength of association relative to the $\chi$—parameter. For a small $\lambda_0$ (large entropy change in bonding) the gelation line cross the binodal at its shoulder as is shown in Fig.(a). This is a point called *critical endpoint* (CEP), because at this point the line of continuous phase transition ends by meeting the first order (discontinuous) phase transition line. The critical point remains intact on the top of the miscibility gap. For a larger $\lambda_0$, the intersection is lifted as in Fig.(b). The tip is called *tricritical point* (TCP), where the line of continuous phase transition changes into the first order line. The critical point still remains. In this situation there is a temperature at which three phases (dilute sol $S_1$, concentrated sol $S_2$ and gel G) coexist. This is a *triple point* temperature. For a still larger $\lambda_0$, the intersection goes further up to form a sharp TCP as in Fig.(c). The critical point disappears. Fig.5 shows the comparison [11] of the theory with the experimental data [13] observed in (polystyrene/carbon disulfide) solution. This figure corresponds to TCP in Fig.4(c). CEP in Fig.4(a) has also been observed for smaller molecular weight polystyrene.

**Multiple Junctions** We next study the multiple junctions carrying the multiplicity $s$ larger than 2. Crystalline polymers are partially cross-linked by microcrystallization involving several chains and form gels with fringed micellar structures. There should be a minimum multiplicity $s_{\text{min}}$ for a crystalline to remain stable. This bound is given by the size of the critical nucleus. Another example of thermoreversible gels with multiple junctions is the ionomers, i.e., neutral polymers with dipolar side groups attached sparsely on the chain backbone. Due to electrostatic aggregation, junction zones
called "multiplet" are formed, but there is a maximum aggregation number $s_{max}$ because chains are closely packed around the multiplets. It is found [14] that multiplicity largely affects the phase behavior; small $s$ gives CEP, while large $s$ gives TCP. There is a marginal value of $s$ separating the two cases. Gels with variable junction multiplicity is studied in detail in [14].

**Mixed Network** When the two components A and B are cross-linked, hetero-networks are formed. Competition between macroscopic phase separation and heterobonding takes place, but another possibility comes out by the reason that the clusters formed are all block copolymers. This is microphase separation transition. In the extreme case, one can even expect the appearance of microphase-separated polymer networks.

In contrast to this case, *interpenetrating polymer networks* (IPN) are formed when cross-links between only the same species are possible. Due to the small entropy of mixing for large molecular-weight polymers, most IPN's are thermodynamically unstable, so that controlling the nonequilibrium morphology is the principal problem with regard to IPN. Our thermodynamic theory [15], however, predicts that there is a possibility for the appearance of stable IPN in a small region above the miscibility gap when the parameter $\lambda_0$ related to the entropy loss is small. Polymers of different species are topologically connected instead of being directly bonded. Such constraints prevent the translational motion of each chain and can lead to microphase formation.

**CONCLUSION**

It has been shown that competing two terms — reaction and mixing — must be considered in the free energy to describe associating polymer blends and solutions. Several new concepts have been introduced that can be reached only if both synthetic aspect and material-properties are simultaneously taken into consideration. But dynamical phenomena of the phase formation still remain unsolved. Polymer association is a problem which is quite new and fundamental, providing many questions yet to be theoretically and experimentally studied.

---

Figure 1. Typical example of the phase diagrams for the associating diblock copolymer blends of relatively short chains \( n_A = n_B = 20 \). MST (broken line) and SP (solid lines) are shown on the temperature-concentration plane. The entire plane is divided into several regions whose characters are indicated by capital letters (see text for details). Two points shown by \((L)\) are Lifshitz points, while those shown by \( e \) and \( e' \) are eutectic points. The existence of a reentrant microphase \( M' \) is one of the remarkable features of the associating systems.

FIG. 2. Phase diagrams on the temperature-concentration plane. The solid (dashed) curves correspond to the binodal (spinodal) curves. See text for details.

FIG. 3. Comparison of the theoretical calculation with the observed phase diagram for polyethylene glycol (PEO) in water.

FIG. 4. Temperature-concentration phase diagram of low-molecular-weight thermoreversible gels.

FIG. 5. Comparison of the calculated phase diagram with the experimental data for at-PS/CS2.
SANS STUDY OF POLYMER CHAINS IN CONFINED SPACE

*Hirokazu HASEGAWA, *Hideaki TANAKA, *Takeji HASHIMOTO and *Charles C. HAN

*Department of Polymer Chemistry
Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto, 606-01 Japan

*Polymers Division
National Institute of Standards and Technology
Gaithersburg, Maryland 20899 U.S.A.

ABSTRACT

The lateral and vertical components of the radius of gyration for a single block copolymer chain in the lamellar microdomain space formed by a mixture of diblock copolymers and homopolymers were investigated by means of small-angle neutron scattering (SANS), and the microdomain structures by small-angle X-ray scattering (SAXS). We used the homopolymers whose molecular weights are much smaller than that of the corresponding chains of the block copolymers so that the homopolymers are uniformly solubilized in the corresponding microdomains. The SANS result suggests that the block copolymer chains in the microdomain space are more compressed in the direction parallel to the interface and more stretched in the direction perpendicular to the interface than the corresponding unperturbed polymer chains with the same molecular weight. With increasing the volume fraction of the homopolymers the thickness of the lamellar microdomains increases. The block copolymer chains were found to undergo an isochoric affine deformation on addition of the homopolymers or with the change of the thickness of the lamellar microdomains.

INTRODUCTION

Block copolymers comprising immiscible polymer pairs undergo microphase separation. Although various microdomain morphologies are possible, the size of the microdomain is limited to the dimension of the block chains due to the connectivity by a covalent bond between the two polymers. The conformation of the single block chain in such a confined space is an important problem to understand the physics of microphase separation. Small-angle neutron scattering (SANS) is a useful technique to investigate this problem. We previously investigated the single chain conformation of block copolymers in the lamellar microdomains formed only by the block copolymers1,2. The results are summarized in Table 1 as well as the results by Hadziioannou et al.3. The results show that the component of radius of gyration of the block chains parallel to the lamellar interface, $R_{g,k}$, (measured value of $R_{g,x}$ as designated in Fig. 1 although it
is an illustration for the case of the block copolymer/homopolymer mixture) is about 70% of that of the unperturbed chain, $R_{gX,0}$, with the same molecular weight. On the other hand, the component of radius of gyration of the block chains perpendicular to the lamellar interface, $R_{gZ,m}$ (measured value of $R_{gZ}$), is about 110% of that of the corresponding unperturbed chain. In consequence, the net radius of gyration of the block chains in lamellar microdomain space, $R_{g,m}$, is about 90% of that of the corresponding unperturbed chain, $R_{g,0}$. Thus the block polymer chains in the lamellar microdomain space is laterally squeezed and longitudinally extended with respect to the interface.

Table 1. Radius of Gyration of Block Chains in Lamellar Domain Space

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>block chain</th>
<th>$M_n$ block $\times 10^4$</th>
<th>$R_{gX,m}$ (Å)</th>
<th>$R_{gZ,m}$ (Å)</th>
<th>$R_{gX,0}$ (Å)</th>
<th>$R_{gX,m}/R_{gX,0}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDI-12</td>
<td>DPS</td>
<td>11.07</td>
<td>33.6</td>
<td>50.4</td>
<td>0.67</td>
<td>3)</td>
<td></td>
</tr>
<tr>
<td>SDI-7</td>
<td>DPS</td>
<td>6.89</td>
<td>33.6</td>
<td>39.8</td>
<td>0.77</td>
<td>3)</td>
<td></td>
</tr>
<tr>
<td>DSI</td>
<td>DPS</td>
<td>4.05</td>
<td>22</td>
<td>36</td>
<td>0.72</td>
<td>48 52 1)</td>
<td></td>
</tr>
<tr>
<td>B-7</td>
<td>DPB</td>
<td>3.34</td>
<td>32</td>
<td>44.3</td>
<td>0.72</td>
<td>2)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1 Schematic representation of block copolymer chains in a lamellar microdomain space. $R_{gX}$ and $R_{gZ}$ denote the component of radius of gyration of the block-chain molecule in the direction parallel and perpendicular to the interface, respectively. The same notations were used for the homopolymer chains in the microdomain space.

In mixtures of poly(styrene-b-isoprene) diblock copolymer (SI) and polystyrene homopolymers (HS) and/or polyisoprene homopolymers (HI) with their molecular weights much smaller than the corresponding block chains, the homopolymers are solubilized in the corresponding microdomains of the block copolymer, and a microdomain structure with a long-range spatial order is formed up to a very high homopolymer concentration.\(^{4,5}\) When both HS and HI are added to SI along the isopleth line, the same morphology can be maintained and only the average spacing of the microdomains (domain spacing) increases with increasing volume fraction of the homopolymers. The experimental evidence that the long-range spatial order is still maintained even after the domain spacing of the mixture exceeds twice of that of the pure block copolymer suggests that the polystyrene (PS) (polyisoprene (PI)) block chains emanating from the opposing interfaces have sufficiently extensive overlapping in the PS (PI) domains and that HS (HI) is more or less uniformly solubilized in the PS (PI) microdomains. The HS (HI) chains do not essentially screen the intermolecular interactions between the PS (PI) block chains. If the HS (HI) chains are localized in the center of the PS (PI) domains and screen the intermolecular interactions of the PS (PI) block chains, the amount of HS (HI) solubilized in the PS (PI) domains is expected.
to vary one by one. Under this condition, the long-range order of the uniformly thick lamellae cannot be attained. The overlap of the block chains and the uniform solubilization of the homopolymers imply that the block chains in such a mixture are stretched more in the direction perpendicular to the interface than those in the pure block copolymer system. Therefore, the single chain conformation of block copolymers in such a system is very interesting. The purpose of this study is to evaluate the lateral and vertical components of radius of gyration, $R_g$ and $R_z$, respectively, for a single block copolymer chain in the lamellar microdomain space, as schematically shown in Fig. 1.

**EXPERIMENTAL**

Table 2 summarizes the characteristics of the polymer samples used for the study of block-chain conformation as a function of the amount of the solubilized homopolymers. Three kinds of mixtures, BC1 to BC3, shown in Table 3 were prepared for the study of the block chain conformation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer*</th>
<th>$M_n \times 10^4$</th>
<th>Weight Fraction of PS</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOKI-12</td>
<td>HPS-HPB block</td>
<td>9.99</td>
<td>0.52</td>
<td>1.03</td>
</tr>
<tr>
<td>B-7</td>
<td>HPS-DPB block</td>
<td>8.49</td>
<td>0.56</td>
<td>1.02</td>
</tr>
<tr>
<td>H-11</td>
<td>HPB homo</td>
<td>0.69</td>
<td>0.00</td>
<td>1.10</td>
</tr>
<tr>
<td>H-12</td>
<td>HPS homo</td>
<td>0.44</td>
<td>1.00</td>
<td>1.06</td>
</tr>
</tbody>
</table>

* HPS: protonated polystyrene, HPB: protonated polybutadiene, DPB: deuterated polybutadiene

Table 3. Composition of Mixtures for the Study on Block Chain Conformation in Lamellar Microdomain Space.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>TOKI-12 (wt%)</th>
<th>B-7 (wt%)</th>
<th>H-11 (wt%)</th>
<th>H-12 (wt%)</th>
<th>$\phi_b^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC1</td>
<td>80.7</td>
<td>19.3</td>
<td>0.0</td>
<td>0.0</td>
<td>1.00</td>
</tr>
<tr>
<td>BC2</td>
<td>29.9</td>
<td>20.1</td>
<td>26.6</td>
<td>23.4</td>
<td>0.50</td>
</tr>
<tr>
<td>BC3</td>
<td>0.0</td>
<td>15.0</td>
<td>42.5</td>
<td>42.5</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*$\phi_b$: volume fraction of block copolymer in a mixture.

In this study, the "contrast matching" technique was utilized so that the scattering arising from the microdomain structures ("domain scattering") can be made insignificant and only the scattering from the isolated deuterated-polybutadiene (DPB) block chains ("molecular scattering") can be observed. The scattering length of a protonated styrene monomer unit for neutrons is between those of a protonated and a deuterated-butadiene monomer unit, and the contrast matching can be achieved when the volume fraction of DPB in the polybutadiene (PB) microdomain is 16.5% according to the calculation. The volume fraction of DPB for all the mixtures in Table 3 is 16.2% which is very close to the calculated value. The volume fraction of block copolymers in the mixtures, $\phi_b$, is 1.00 for BC1, 0.50 for BC2 and 0.15 for BC3. The films of the mixtures for both studies were prepared by casting from 10 wt% solutions in toluene at 30 °C. As expected from the fact that the volume fractions of polystyrene (PS) component in all these
mixtures are close to 0.5, those cast films were found to have the microdomain structure of alternating lamellae with the preferential orientation of their interfaces parallel to the film surfaces from small-angle X-ray scattering (SAXS) analyses.

SAXS measurements give information about the microdomain structures, e.g., morphology, domain spacing, orientation of the microdomains, etc. The corrected SAXS profiles were obtained by the method as described elsewhere. SANS measurements of the films were done with the SANS instrument equipped with a two-dimensional detector at the NIST research reactor. SAXS and SANS measurements were done with two different geometries; incident X-ray or neutron beam normal to the film surface (THROUGH) and parallel to the film surface (EDGE). Due to the preferential orientation of the lamellar microdomains with respect to the film surface, the EDGE scattering patterns are anisotropic while the THROUGH patterns are isotropic. The dimension of the DPB block chains in the direction parallel to the interface can be obtained from the THROUGH data and both of those in the directions parallel and perpendicular to the interface can be obtained from the EDGE data.

RESULTS AND DISCUSSION

The SAXS EDGE profiles of the three films listed in Table 3 are shown in Fig. 2. All the profiles show higher-order maxima at the peak positions which are integer multiples of that of the first-order peak, suggesting the existence of the alternating lamellar microdomains with a long-range spatial order. Even BC3 in which $\phi_b$ is only 0.15 shows a highly regular structure. Average domain spacing evaluated from the first-order peak increased from 440 Å ($\phi_b = 1.00$) to 630 Å ($\phi_b = 0.5$) and 1100 Å ($\phi_b = 0.15$) by adding the homopolymers.

Figure 2  SANS intensity distribution curves obtained for the cast films of the polymer mixtures listed in Table 3 with the incident beam parallel to the film surface and scanning direction normal to the film surface (EDGE). $q = (4\pi/\lambda) \sin \theta$ (2θ: scattering angle)
Fig. 3 shows the SANS profiles from the films before the correction for the incoherent scattering. EDGE 0 in the figure denotes the scattering intensity distribution in the direction perpendicular to the film surface and EDGE 90 parallel to the film surface for the EDGE data. The EDGE 0 profiles of the three films show the scattering maxima caused by the long-range order of the lamellar domains, indicating the contrast matching was not perfect. Although the peak intensity of BC1 due to the microdomains is very effectively suppressed to less than 1/100 of that measured for pure TOKI-12 film by using the contrast matching technique, the matching was still imperfect and insufficient for the evaluation of $R_g$. The reason for the imperfect matching was discussed elsewhere$^2$, on the basis of insufficient overlapping of the deuterated species within the PB microdomains. The insufficient overlapping causes concentration fluctuations of the DPB block chains in the PB domains. The concentration fluctuations give rise to the "molecular scattering" as predicted by the RPA$^3$ which, in turn, is responsible for the imperfect matching as it causes an excess scattering. Note that the fluctuations are not averaged out to zero in the scattering process except at $q = 0$ and hence cause the excess scattering or the imperfect matching at $q \neq 0$. Note also that this "molecular scattering" is different from that caused by the two-phase domain structure (the "domain scattering"). The domain scattering itself should be cancelled by the contrast matching.

However, our previous interpretation$^2$ is still insufficient and misleading in that the imperfect matching or the excess scattering occurs even in the case in which the labeled polymer coils have a sufficient overlapping. Even in this case there are thermal concentration fluctuations of the labeled chains in the PB domains in the length scale shorter than the radius of gyration of the PB coils. They cause the excess scattering and the imperfect matching. In our previous paper$^2$ the maximum in the EDGE 0 profile of BC1 in Fig. 3 was denoted as that caused by the "domain scattering". More rigorously this maximum should be described as that interference of the "molecular scattering" but not the "domain scattering" arising from the PB domains arranged in the one-dimensional paracrystal lattice$^{10}$. 

--- 575 ---
Therefore, only the lateral dimension of the block chains, $R_{gx}$, was evaluated by analyzing the THROUGH and EDGE 90 data obtained for the cast films for which the domain scattering intensity is not significant. The Guinier plots for these mixtures showed reasonably linear regions, from the slopes of which the experimental value of the one-dimensional component of radius of gyration of the DPB block chains in the direction parallel to the lamellar interface, $R_{gx,m}$ ($=R_{gy,m}$), was obtained and the results are listed in Table 4. It should be noted that $R_{gx,m}$ decreases with increasing the volume fraction of the homopolymers.

Table 4. Comparison of Lamellar Spacing and Radius of Gyration of Block Chains in Lamellar Microdomain Space.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Domain Spacing D (Å)</th>
<th>$R_{gx,m}$ (Å)</th>
<th>$R_{gy,m}$ (Å)</th>
<th>$R_{gz,m}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC1</td>
<td>440</td>
<td>1.0</td>
<td>32</td>
<td>65</td>
</tr>
<tr>
<td>BC2</td>
<td>630</td>
<td>1.4</td>
<td>28</td>
<td>71</td>
</tr>
<tr>
<td>BC3</td>
<td>1100</td>
<td>2.5</td>
<td>20</td>
<td>130</td>
</tr>
</tbody>
</table>

$R_{gx,0} = 44.3$ Å for the corresponding unperturbed chain.

$R_1 = D/D_{BC1}$; $R_2 = (R_{gx,m}/R_{gz,m,BC1})^2$; $R_3 = R_{gz,m}/R_{gz,m,BC1}$

Evaluation of the component of radius of gyration of DPB block chains in the direction perpendicular to the lamellar interface, $R_{gz,m}$, was carried out on the basis of the following principle. If the lateral dimension of the lamellae is much larger than their thickness, as found in our experimental conditions, the perturbation of the molecular scattering due to the interference from the periodic domain structure in the one-dimensional lattice occurs only in the direction of Oz axis, the scattering in any other directions being essentially free from the perturbation and reflecting the true molecular scattering (see Fig. 1). Therefore, the perturbation is significantly reduced by randomizing the orientation of the lamellar microdomains and by detecting the scattering in a given direction. In this condition the molecular scattering becomes dominant to allow the analysis of the average radius of the overall labelled chains $R_{g,m}$ by the Guinier plot.

$$R_{g,m}^2 = 2R_{gx,m}^2 + R_{gz,m}^2$$  \hspace{1cm} (1)

The $R_{gz,m}$ can be determined from the separately determined values of $R_{g,m}$ and $R_{gx,m}$.

SANS profiles were obtained with the powdered specimens for each of the three mixtures which were made by pulverizing the cast films of BC1 to BC3 at liquid nitrogen temperature. The perturbation was significantly reduced by randomizing the orientation of the lamellar microdomains as seen in Fig. 4. Fig. 4 shows the SANS profiles of the powdered specimens of BC1 to BC3. The scattering peaks observed in the EDGE 0 profiles of the cast film in Fig. 3 are remarkably suppressed in those of the powdered specimens in Fig. 4. Thus, the molecular scattering is dominant in the profiles of the powdered specimens to allow the analysis by Guinier plots. Radius of gyration of the DPB coils ($R_{g,m}$) obtained for the powdered specimens was 65 Å for $\phi_b = 1.00$, 71 Å for $\phi_b = 0.50$ and 130 Å for $\phi_b = 0.15$. $R_{gz,m}$ was calculated from these experimental values of $R_{g,m}$ and previously obtained $R_{gx,m}$ using equation (1), and the results are listed in Table 4.
As listed in Table 4, the ratio, \( R_1 \), of the average domain spacing for the mixture containing a given amount of homopolymers to that for the mixture containing no homopolymers, i.e. \( \phi_b = 1.00 \), \( D/D_{BC1} \), the ratio, \( R_2 \), of the inverse square of the component of radius of gyration parallel to the interface for the mixture with a given \( \phi_b \) to that for the mixture with \( \phi_b = 1.00 \), \( (R_{g,m})^{-2}/(R_{g,m,BC1})^{-2} \), and the ratio, \( R_3 \), of the component of radius of gyration perpendicular to the interface for the mixture with a given \( \phi_b \) to that of the mixture with \( \phi_b = 1.00 \), \( R_{g,z,m}/R_{g,z,m,BC1} \) are the same within the experimental error. This implies that the block chains with the laterally squeezed conformation undergo an isochoric affine deformation on addition of the homopolymers, the expansion of lamellar thickness giving the linear extension of the block chains perpendicular to the interface, and the corresponding contraction of the chains parallel to the interface.

![Figure 4: SANS profiles obtained for the powdered specimens of (a) BC1, (b) BC2 and (c) BC3 (incoherent scattering not corrected).](image)

REFERENCES

MICROSCOPIC VIEW OF THE VOLUME PHASE TRANSITION ON WEAKLY CHARGED TEMPERATURE SENSITIVE POLYMER GELS

Mitsuhiro Shibayama* 1), Toyoichi Tanaka2), Charles C. Han3)

1) Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan
2) Department of Physics and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.
3) National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.

ABSTRACT

The static structure factor, I(q), for polyn-isopropylacrylamide-co-acrylic acid) (NIPA/AAc) gels was investigated in terms of small-angle neutron scattering (SANS), where q is the magnitude of the scattering vector. The static structure factor for NIPA/AAc gels was well described by a Lorentz type scattered intensity function at temperatures below 34°C which was near the so-called Θ temperature of NIPA in D2O. At higher temperatures, the static structure factor had a distinct scattering maximum although the gel was still in a highly swollen state. The scattering maximum was located around q = 0.02Å⁻¹ and was temperature and concentration dependent. The appearance of the peak indicates strong concentration fluctuations in the system. The static structure factors were analyzed quantitatively with the theory of Borel and Ershkovich [Macromolecules, 1988, 21, 3240] for polyelectrolyte solutions in a poor solvent.

INTRODUCTION

Polymer gels usually consist of a polymer network and a solvent. The interaction between the polymer network and the solvent determines the size (volume) of the gel. If the solvent molecules have an attractive interaction with the solute, i.e., the polymer network, the gel swells. When the interaction becomes repulsive, which is typically attained by changing temperature and/or by changing the solvent composition, the gel shrinks. This transition is called as the volume phase transition.1,2) The volume phase transition can be either continuous or discontinuous depending on the combinations of interactions3). For neutral polymer networks in a solvent, there is a balance between the Flory-type mixing free energy and the elastic free energy, which determines the volume of gel. In this case, the transition is continuous or a slightly discontinuous. However, if a small portion of the polymer networks is substituted by ionizable groups, the transition becomes discontinuous4). This is due to a strong contribution of the osmotic free energy of the counter ions in the gel. In other words, the Donnan potential between inside (immobile ions on the chain and mobile counter

* To whom correspondence should be addressed.
ions) and outside (mobile ions) of the gel plays a leading role to determine the size of the gel.

The microscopic view of polymer gels have been studied by dynamic light scattering\textsuperscript{5}, small-angle X-ray (SAXS)\textsuperscript{6} and neutron scattering (SANS)\textsuperscript{7-9} techniques. Tanaka observed a critical phenomenon of acrylamide gel by dynamic light scattering\textsuperscript{5}). When the temperature was lowered to -17°C, a divergence of the correlation length and the scattered intensity was observed. Geissler et al. studied the crosslinking density dependence of the gel networks\textsuperscript{8}). We studied the concentration fluctuations of gels undergoing a volume phase transition.\textsuperscript{10}) In the case of N-isopropylacrylamide homopolymer gels (NIPA gel), a continuous volume phase transition was observed from a swollen state to a collapsed state at 34.6°C. This corresponds to the divergence of the correlation length and the susceptibility, i.e., the scattered intensity at \(q = 0\), where \(q\) is the magnitude of the scattering vector. The critical exponents for the correlation length and the susceptibility were about 0.6 and 1.2, indicating that the nature of the critical phenomenon of the volume phase transition of gels is classified to a three dimensional Ising model.\textsuperscript{11}) In the case of partially ionized NIPA gels, which were obtained by co-polymerizing NIPA monomers with a small amount of acrylic acid (AAc) monomers, a discrete volume transition was observed\textsuperscript{4}). The microscopic structures of these gels were found to depend strongly on the temperature and the polymer concentration. Because of a strong hydrophobicity of NIPA molecules, NIPA polymers dissolve in water at temperatures lower than the so-called Θ temperature, but precipitate above this temperature. Therefore this system has a lower critical solution temperature (LCST) behavior.

In spite of a large number of investigations on the volume phase transition of these kinds of gels, microscopic view of the gel and the transition has not been well elucidated. Here we report the temperature and concentration dependence of the static structure factor for poly(N-isopropylacrylamide-co-acrylic acid) (NIPA/AAc) gels obtained by small-angle neutron scattering (SANS). The details of the analyses are presented elsewhere.\textsuperscript{12})

**EXPERIMENTAL**

**Sample Preparation**

7.46g of NIPA, 0.2306g of AAc, and 0.1329g of N,N'-methylenebisacrylamide, and 43mg of ammonium persulfate were mixed with 100 ml of heavy water (D\textsubscript{2}O). After complete dissolution, the solution was degassed and cooled in a refrigerator for about 30 min. The solution was kept in a temperature controlled water bath at 20°C and then 480ml of N,N,N',N'-tetramethylmethylenediamine was added to initiate gelation and polymerization. Thus a NIPA/AAc copolymer gel having 668mM of NIPA and 32mM of AAc was prepared after the gelification at 20°C for 20 hours. After washing with D\textsubscript{2}O, the gel was sifted with a 500mm sieve and dried completely. The prescribed amounts of the gel of eight different kinds were mixed with D\textsubscript{2}O and kept in weighing bottles until the gels became homogeneous and reached constant weights, then transferred into SANS cells and sealed completely by covering the both sides with ca. 1.6 mm-thick quartz windows and rubber rings. Thus eight samples for SANS were prepared. The SANS cell was made of cylindrical-shaped brass of ca. 25 mm inner diameter and 22.5 mm long.

**Small-angle Neutron Scattering**
The small-angle neutron scattering (SANS) experiments were conducted on the 8m-SANS facility at the National Institute of Standards and Technology. Neutron beams were monochromated with a velocity selector to a 9Å-beam and then collimated with a focusing collimation system. The details of the optical setup and the detection system were described by Glinka et al.\textsuperscript{13}. The details of the experiments were the same to the studies reported elsewhere.\textsuperscript{10,12}

RESULTS

Figure 1 shows the swelling-shrinking curve for NIPA/AAc gels (open circles) as well as the concentrations of the samples used for SANS (dashed lines). As discussed in the previous section, each sample was sealed in a quartz cell. Therefore the concentration of each sample is fixed (isochore). In the atmospheric condition, i.e., the isobar condition, the gel swells at temperatures lower than 50.2°C, and shrinks discontinuously at this temperature as shown with the open circles in the figure. Above this temperature, the gel is in the fully shrunken state. This swelling-shrinking transition was reversible with about 2°C hysteresis.

![Swelling-shrinking curve for NIPA/AAc gels (open circles). The dashed lines indicate the paths of the temperature dependent SANS experiments for samples G1 to G8.](image)

Figure 2 shows the SANS profiles of G1 measured at several temperature. At low temperatures, e.g., 25°C and 30°C, the profile is a monotonically decreasing function. By increasing temperature, however, a distinct peak started to appear around q = 0.02Å\textsuperscript{-1} between 35 to 40°C. By further increasing temperature, the peak intensity increased. A similar trend was observed in all samples having different concentrations.

DISCUSSIONS

Concentration dependence of the correlation length
At low temperatures, D$_2$O is a good solvent for NIPA. Therefore the SANS intensity curves are similar to those for NIPA homopolymer gels at temperatures much lower than the critical temperature. The correlation length, $\xi$, was estimated from the structure factors, $I(q)$, at low temperatures since $I(q)$ was well described with the Ornstein-Zernike form:

$$I(q) = \frac{I(0)}{1 + \xi^2 q^2}$$

(1)

$\xi$ was a decreasing function of $\phi$ and was roughly scaled as,

$$\xi = \phi^{-0.53} \quad \text{for } \phi > 0.017$$

(2)

This exponent is quite different from those for the NIPA homopolymer gels (-1.1 to -1.2) and NIPA homopolymer solutions (-3/4).10

**Long Spacing of the Concentration Fluctuations**

The concentration and temperature dependencies of the long spacing of the concentration fluctuations are also of interest. We define the long spacing, $D$, as follows,

$$D = 2\pi/q_m$$

(3)

where $q_m$ is the maximum of the magnitude of the scattering vector, $q$. As shown in Figure 1, $q_m$ appears at temperatures above 35°C. At 46°C, this kind of scattering maximum was observed in all the samples. $D$ varies from 480Å to 305Å by increasing $\phi$, and is roughly scaled by

$$D \sim \phi^{-0.27} \quad \text{for } 0.0236 \leq \phi \leq 0.107 \quad \text{at } 46^\circ\text{C}$$

(4)
The appearance of the scattering maximum originates from strong concentration fluctuations created by antagonistic interactions of the Coulombic repulsive interaction between AAc segments and the hydrophobic attractive interaction of NIPA chains.

Quantitative Analyses of the scattered intensity functions

In this section, we examine the structure factor more quantitatively by taking into account the fact that a partially ionized polymer solution is a three component system composed of the solvent, polyions, and counter ions. There exist two characteristic screening lengths, i.e., electrostatic screening length (Debye screening length, $\kappa^{-1}$) and Edwards screening length, $\xi$. Borue and Ershov proposed a scattering function for weakly charged polyelectrolytes in the semi-dilute regime based on the random phase approximation.\textsuperscript{14} This theory is a Debye-Hückel type theory for polyelectrolytes and predicts the scattering behavior of polyelectrolytes in a poor solvent. A similar theory was proposed by Leibler et al.\textsuperscript{15} The structure factor is given by

\[ S(x) = C_1 \frac{(x^2 + s)}{(x^2 + t(x^2 + s) + 1) \left( \frac{4 \pi \lambda_B}{a} \phi \alpha^2 \right)^{-1/4}} \]  \hspace{1cm} (5)

where $x$, $t$, and $s$ are the reduced scattering vector, the reduced temperature and the reduced charge concentration as will be defined later. $C_1$ is a proportional constant. When $s$ is large, the Debye screening length becomes short and the polymer chains behave as if they were neutral polymers. The reduced scattering vector is given by using the characteristic scale of screening of Coulombic interaction by ideal Gaussian chains, $r_0$, as follows,

\[ x \equiv r_0 q \]  \hspace{1cm} (6)

\[ r_0 = a \left( 1 + \left[ \frac{1}{2 \phi} (1 - 2 \chi) \right]^{1/2} \right)^{1/4} \left( \frac{4 \pi \lambda_B}{a} \phi \alpha^2 \right)^{-1/4} \]  \hspace{1cm} for $\chi < \frac{1}{2}$

\[ r_0 = a \left( \frac{4 \pi \lambda_B}{a} \phi \alpha^2 \right)^{-1/4} \]  \hspace{1cm} for $\chi \geq \frac{1}{2}$

(7)

where $a$ is the segment length, $\phi$ the volume fraction of polymer network, and $\chi$ the Flory interaction parameter. $\alpha$ and $\lambda_B$ are the degree of ionization and the Bjerrum length, respectively. The reduced charge concentration $s$ is defined with the Debye length, $\kappa^{-1}$ as follows,

\[ s \equiv \kappa^2 r_0^2 \]  \hspace{1cm} (8)

and

\[ \kappa^2 = 4 \pi \frac{\lambda_B}{a^3} \sum_{i} \left( z_i \phi_{s,i} + \alpha \phi \right) \]  \hspace{1cm} (9)

where $\phi_{s,i}$ is the salt concentration of kind $i$ having the valency $z_i$. The reduced temperature stands for the solvent quality. For a larger $t$ value, the solvent is good for the solute, and the solvent becomes a poor solvent by decreasing $t$. $t$ is defined by
\[ t = -12 \left( \frac{r_0}{a} \right)^2 \frac{h}{a^3} \phi \]  

\[ h = -a^3(1 - 2\chi) - 3B_3 \phi \]  

where \( B_3 \) is the third virial coefficient.

For \( r_0^{-1} \gg \kappa \), eq 5 predicts an appearance of the scattering maximum at \( q_m \).

\[ q_m = (r_0^{-2} - \kappa^2)^{1/2} \]  

If \( \kappa \) is much larger than \( r_0^{-1} \), the screening due to the salt ions become dominant, and the structure factor becomes similar to the one for neutral polymer solutions.

![Figure 3. Result of the curve fitting for G1 (\( \phi = 0.196 \)) at several temperatures.](image)

All of the observed SANS intensity functions were analyzed, based on the theory described above. Figure 3 shows an example of the result of the curve fitting, which is for G1 (\( \phi = 0.196 \)) at several temperatures. The curve fitting was conducted by fixing the parameter \( r_0 \) and floating three parameters, \( s \), \( t \), and the proportional constant \( C_1 \). \( r_0 \) was estimated by eq 7 where the dielectric constant \( \varepsilon \) for heavy water at 20°C was chosen to be 80,16) and no temperature dependence was assumed. The value of \( a \) was chosen to be 8.12Å.17) The parameter \( \chi \) was estimated with the following equation

\[ \chi = A(1 - \frac{\Theta}{T}) + \frac{1}{2} \]  

where a set of parameters \( A = -25 \) and \( \Theta = 306.5K \) was employed which was obtained for the NIPA gels in D_2O.10) The acrylic acid was assumed to be fully ionized, i.e., \( \alpha = 0.0457 \). As can be seen in the figure, the curve fitting was quite successful except for those at 40°C and 44°C. The same analysis was carried out for all samples at all
temperatures. All the structure factors observed in this work were classified to two types with and without the peak maximum. We define the temperature at which the scattering maximum appears as $T_{\text{peak}}$.

Figure 4 shows (a) the scattered intensity at $q = 0$, $I(0)$, (b) the Debye length, $\kappa^{-1}$, and the characteristic length, $r_0$, and (c) the solvent quality parameter, $h/a^3$ as a function of temperature for G1. Figure 4(a) shows a steep increase in $I(0)$ around $T_{\text{peak}}$. $I(0)$

![Graphs showing temperature dependence](image)

Figure 4. Temperature dependence of (a) $I(q)$, (b) $r_0$ and $\kappa^{-1}$, and (c) $h/a^3$.

![Diagram of state](image)

Figure 5. Diagram of state for G1. $t$ and $s$ denote the reduced temperature and the reduced charge concentration, respectively. The solid curve indicates the spinodal line.

increases rather linearly with $T$. In Figure 4(b), although $\kappa^{-1}$ is smaller than $r_0$ at low temperatures, it starts to increase remarkably at around $T_{\text{peak}}$ and exceeds $r_0$ at 38°C.
The temperature at which I(0) start to increase coincides with the temperature at which $kT$ exceeds $r_0$. Figure 4(c) shows that $h/a^3$ is negative at temperatures lower than $T_{\text{peak}}$ and positive at temperatures above this temperature.

Figure 5 shows the diagram of state for G1 in terms of the reduced parameters, $t$ and $s$. The solid line in the figure indicates the spinodal line. The experimental data points are mapped on the diagram with open circles. At $T < T_{\text{peak}}$, the gel is in more or less stable state where the solvent is good for the polymer network and/or the Coulombic potential is strong enough. When $T$ becomes higher than $T_{\text{peak}}$, the solvent becomes poor to the network and the hydrophobic interaction overcomes the Coulombic repulsive interaction, resulting in the occurrence of either microphase separation (for $t < 1$) or macrophase separation (for $t > 1$).

The details of the analyses are reported in ref. 12. A re-examination of the validity of the BE theory for polyelectrolyte gels will be discussed elsewhere. 18)

CONCLUDING REMARKS

The static structure factor for weakly ionized polymer networks was investigated with SANS as a function of polymer network concentration and temperature. The structure factor was well described with an Ornstein-Zernike type scattered intensity function at temperatures lower than $T_{\text{peak}}$. At higher temperatures, the structure factor was well predicted by the theoretical structure factor proposed by Borue and Erukhimovich. The fitted parameters indicate the nature of the polyelectrolyte gels in a poor solvent.

REFERENCES

3. Y. Li, PhD Dissertation, Physics Department, Massachusetts Institute of Technology (1989).
DIFFRACTOMETER FOR NEUTRON CRYSTALLOGRAPHY IN BIOLOGY
-JAPANESE PROJECT-

Nobuo NIIMURA

Advanced Basic Research Center, Tokai Research Establishment, JAERI,
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11, Japan
and
Laboratory of Nuclear Science, Tohoku University, Mikamine 1-2,
Taihaku-ku, Sendai, 982, Japan

ABSTRACT

Since the structure-function relationship of proteins is dominated by the behavior of hydrogen atoms, it is important to know the structural information of hydrogen atoms. Neutron diffraction provides an experimental method of directly locating hydrogen atoms. So, we have had a project to construct the dedicated diffractometer for the neutron crystallography in biology at JRR-3M in JAERI (Japan Atomic Energy Research Institute). The diffraction intensity from the protein crystal is weaker than that from most of inorganic materials. In order to overcome the intensity problem, three items should be considered carefully. Those are (1) how to get a large single crystal, (2) how to get intense neutron flux on a sample position, and (3) how to get a genuine detector system.

INTRODUCTION

The x-ray diffraction of single crystals has supplied knowledge about the atomic structure of proteins, viruses, t-RNA and DNA. Since the structure-function relationship of proteins is dominated by the behavior of hydrogen atoms, it is important to know the structural information of hydrogen atoms. However, it is difficult for x-ray crystallography in biology to give the structural information of hydrogen atoms. On the other hand, neutron diffraction provides an experimental method of directly locating hydrogen atoms. Moreover, neutron diffraction has several distinctive advantages over x-ray one, and they are summarized as follows:

Neutron diffraction can locate light atoms such as hydrogen and deuterium. Since the scattering length of hydrogen is different from that
of deuterium, hydrogen and deuterium could be distinguished from each other, and this is useful to study H/D exchange, contrast variation with different D$_2$O/H$_2$O mother liquid, and so on. Nitrogen, with its greater scattering length, can be distinguished from carbon and from oxygen. The crystals are not damaged by neutrons as they are by x-rays. The higher-angle scattering data should be more easily observable for neutrons than for x-rays.

The most serious disadvantage of neutron diffraction is the low flux of neutrons irradiated on the sample specimen. The diffraction intensity is written as

$$ I \propto I_0 \cdot V \cdot A / (v_0)^2, $$

where $I$, $I_0$, $V$, $A$ and $v_0$ are diffraction intensity, incident neutron intensity, the volume of the sample specimen, detector area subtended by the specimen and the volume of the unit cell, respectively. Normally the unit cell dimension of the protein crystal is about ten times larger than that of most of the inorganic materials. Because of this term, diffracted intensity from the protein crystal becomes weaker, though structural form factors gain the diffracted intensity.

We have had a project to construct the dedicated diffractometer for the neutron crystallography in biology at JRR-3M in JAERI (Japan Atomic Energy Research Institute). The diffractometer will be called as BIX, tentatively.

In order to overcome the intensity problem, three items have been considered carefully. Those are (1) how to get a large single crystal, (2) how to get intense neutron flux on a sample position, and (3) how to get a genuine detector system.

This paper reports the tentative and general view of the project.

**How to get a large single crystal**

It is said that the neutron flux at JRR-3M is about one half of that at BNL (Brookhaven National Laboratory) and about one fifth of that at ILL (Institute of Laue-Langevin). The usual volumes of protein single crystals used at BNL and ILL are about 1 mm$^3$ and 3 mm$^3$, respectively. If the diffractometer of the same performance as the one of BNL or ILL is available in JRR-3M, the sample of about 5 or 6 mm$^3$ in volume is necessary, in principle. To get such a large single crystal must be a hard job, but not impossible.

Recently Ataka et al. have developed the method to grow a lysozyme single crystal of more than 200 mm$^3$ in volume easily$^1$. Dr. Ataka will join our project and he will continue developing the method and try to apply it for the other proteins. We could also observe the initial stage of the lysozyme crystal growth by using the small angle
neutron scattering method\textsuperscript{2}), and this also helps us to know the general mechanism of the protein crystal growth. The desire to grow a large single crystal of biomolecules such as protein and DNA is accelerated day by day.

However, since there are some proteins which never grows as a large single crystal as used in the neutron diffraction, we will design and develop the special equipment which composes a large crystal by gathering several small single crystals and aligning their crystal axes. The alignment operation could be carried out with use of neutron diffraction and optical microscopy. The fact that crystals are not damaged by neutron irradiation is very convenient.

\textbf{Intense neutron flux}

In order to get intense neutron flux on a sample position for an inelastic neutron scattering instrument, it is a normal way to adopt not only vertically but also horizontally focussing monochromator as far as the Q-resolution is tolerable. However, in a single crystal diffractometry, no or slight vertical focussing monochromater method is applied so far because of the serious Q-resolution.

We would like to develop a new type of a focusing monochromator even in the case of the single crystal diffractometry. In this method, an assembly of monochromator is composed of several different kinds and pieces of crystal and is curved as refracted neutrons of different kinds of wavelength are focused onto the sample as shown in Fig.1 (a).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Multi-wavelength method. (a) in real space and (b) in reciprocal space}
\end{figure}
M1, M2 and M3 are monochromator crystals, the interplanar distances of which are d1, d2 and d3, respectively. Neutrons of three different wavelength \(\lambda_1, \lambda_2\) and \(\lambda_3\) impinge onto the specimen. Neutrons of each wavelength could be enough collimated, and we could expect the fine angular dispersion as far as the conditions as a monochromator of each piece of crystals such as the size, mosaicity and so on are sufficiently arranged. Because of the multi-wavelength, the neutron flux irradiated onto the sample should be absolutely increased, although the diffraction pattern becomes more complicated.

Fig.1(b) shows the diffraction principle of the multi-wavelength method in the reciprocal space. Strictly speaking, the directions of the incident vectors, A1O, A2O and A3O, are not the same, but they are drawn in the same direction as an approximation in the figure. While a crystal rotates with a unit angle, each Ewald sphere crosses the reciprocal lattice points and Bragg reflection occurs. Because of the multi-wavelength, the number of Bragg reflections diffracted onto the area detectors increases about three times larger than that of the normal cases. At the same time, however, the probability that Bragg reflections overlap each other increases. So, data acquisition procedure becomes very important and this will be discussed in the later section.

A detector system

In order to enlarge the solid angle subtended by a sample, the plural area detectors are equipped. At the first stage, 3 conventional gas-filled proportional detectors (ORDELAL MODEL 2250N; active area 25cm x 25cm; pixel size 2mm x 2mm) will be utilized and they cover 8.3 % of the whole effective solid angle subtended by the specimen.

In the project, the development of the more genuine detector such as an imaging plate (IP) for neutrons which is common to x-ray diffractometry is included. The x-ray diffractometry has been extraordinarily grown up since the practical use of the IP started. Although there were several trials of the application of the IP for neutron diffractometry, the practical use for it cannot yet be realized. Since the recording material BaFX:Eu2+(X=Cl,Br,I) does not interact with neutrons, neutron converter is necessary as a component, and Gd has been considered and tested as a converter material so far. If we consider the energy and the flight path length of the secondary particles of nuclear reaction in the converter, elements which react with neutron such as \((n,\alpha)\), \((n,p)\) and \((n,\beta)\) might be more effective. In any way, the kind, shape and size of the neutron converter and its combination with the recording material must be considered and tested.
Data acquisition procedure

The proper data acquisition procedure enables us the avoidance of overlappings of Bragg reflections. If reflected neutrons onto area detectors should be accumulated within the wide crystal rotation angle, there would be many overlappings of Bragg reflections. While a specimen crystal is stationary, the least overlapping of Bragg reflections could be expected. After the measurement in a certain interval, all the data are transferred to the outer memory, and then the data on the area detector are cleared and the specimen is rotated in a unit of angle and a new measurement starts. As far as lattice constants and the geometrical orientation of the specimen and the profile of the reflection are known, neutron events on the area detector could be assigned in principle. While the new measurement is carried out, the transferred data are assigned to the diffraction indices. This procedure is repeated in a certain step of crystal rotation.

Interference with other diffractometer

The beam port where the BIX will be settled is 1G-A as a first candidate. At the downstream1G-A, a high resolution powder diffractometer (HRPD) has been already equipped. The least interference must be necessary for the installation of BIX.

---

Fig.2 Intensity loss at HRPD and gain at BIX.
The cross section of 1G beam is 8 cm in height and 4 cm in width and the full area is now used for the HRPD. For the BIX monochrometer, the bottom of the half height is allowed to be used, and the available area for the BIX monochrometer depends on how it interferes with HRPD. Fig.2 shows the intensity fraction decreased by the BIX copper monochromator (1.1mm in thickness) and the intensity gain of the BIX as a function of BIX monochrometer area (cm²).

The general performances

The general performances of the BIX are summarized in Table.

<table>
<thead>
<tr>
<th>beam tube</th>
<th>1G-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>monochromater</td>
<td>Graphite (002), Silicon (311), Copper(002), Germanium(311), Aluminium(200)</td>
</tr>
<tr>
<td>monochromater Bragg angle</td>
<td>θ=32, 44</td>
</tr>
<tr>
<td>intensity at the sample position</td>
<td>$10^6-10^7$ n cm⁻² s⁻¹</td>
</tr>
<tr>
<td>maximum beam size at sample</td>
<td>10mm x 10mm</td>
</tr>
<tr>
<td>incident wavelength</td>
<td>λ=0.9-2.5 Å</td>
</tr>
<tr>
<td>detector type</td>
<td>ORDERA MODEL 2250N (x3; tentatively)</td>
</tr>
<tr>
<td>detector resolution</td>
<td>2mm x 2mm</td>
</tr>
<tr>
<td>sample to detector distance</td>
<td>60cm-100cm</td>
</tr>
<tr>
<td>observable d range</td>
<td>0.52 Å &lt; d &lt; 9.4Å</td>
</tr>
</tbody>
</table>

References
STRUCTURE STUDY FOR
THE COMPLEX OF HU PROTEIN AND DNA

Ichiro TANAKA, Nobuo NIIMURA, Isao TANAKA, Mikio KATAOKA,
Ken-ichi MIHARA, Fumio TOKUNAGA, Kazuei MITA

Laboratory of Nuclear Science
Faculty of Science, Tohoku University
Mikamine, Taihaku, Sendai, Miyagi, 982 Japan

*Department of Polymer
Faculty of Science, Hokkaido University
Kita, Sapporo, Hokkaido, 060 Japan

**Department of Biology
Faculty of Science, Osaka University
Machikaneyama, Toyonaka, Osaka, 560 Japan

***Biology Division
National Institute of Radiological Science
Anagawa, , Chiba, 280 Japan

ABSTRACT

The small angle X-ray and neutron scattering experiments have revealed the structure of the complex of DNA-binding protein HU and DNA with 20 base pair long in solution. By comparing observed Rg (Radius of gyration) of the complex with calculated Rg of the model, we have concluded that HU protein binds DNA in such a manner that the protein bends the rod-like DNA, and that the binding is rather cooperative. This is the first evidence on the structure of HU-DNA complex obtained by the diffractive method in vitro. These findings give us the view that HU protein might facilitate the DNA's dynamical reactions in a cell by winding DNA like an enzyme, and that there might be a possibility that cells turn on and off the enzymatic actions by changing the concentration of HU protein.

INTRODUCTION

Living creatures are classified into two groups whether they have nuclear membrane or not
in their cells, and they are eucaryotes or procaryotes respectively.

The DNA double helix in eucaryotic cell would span thousand times of the cell nucleus if it were stretched out. Histones play an important part in packing this very long DNA molecule in an orderly way into a nucleus of only a few micro-meters in diameter. The fundamental packing unit is known as the nucleosome, a complex of histone protein octamer and DNA.

In procaryotes, although the genome is much smaller, it has been made clear that there is some kind of DNA packaging. Following the gentle lysis of cells, chromosomes can be isolated in a folded and supercoiled conformation as complexes of proteins and DNA just close to in vivo. Some of these proteins exhibits several histone-like properties clearly. These small basic proteins have been shown to form bead-like structures along the double-stranded DNA in a manner similar to the histones, which had been confirmed by the electron microscopy. Such proteins have been called as HU protein in common name.

In 1984, the crystal structure of HU protein had been determined by X-ray crystallography[1][Fig.1&2]. In crystal HU proteins form dimer. It is assumed that the two protuberant arms bind the phosphate back bone or major groove of DNA double helix, though the structure of several amino acid residues in the arm has not been able to be determined because of the positional or dynamical disorder in the crystal. However, nobody knows the structure in the form of the HU-DNA complex.

---

**Fig. 1:** Structure view from two sides of the dimer of HU protein, determined by X-ray crystallography. Principal carbon atom is shown to be bound together in the order of amino acid sequence. Note that DNA with HU protein is only putative, and that the complex structure at the atomic level has not been ever carried out.

**Fig. 2**

Especially structure study of HU-DNA complex, unlikely to histone-DNA complex (nucleosome), is very attractive because it has been reported that HU protein is a transcription and replication factor of active DNA\textsuperscript{9,30,31} according to some biochemical experiments. We can expect to clarify the physiological functions of HU protein towards DNA by getting the structure information of HU-DNA complex.

**SAMPLE PREPARATION & EXPERIMENT**

a) **preparation of HU protein**: We obtained the source of HU protein, a bacterium *Bacillus stearothermophilus* of about 700 (gram) in wet mass, which was collected twice after a large scale fermentation of 200 (liter). Next, we extracted contents from the bacterial cells by breaking the cell wall with use of pressure difference, then centrifuged them to get a crude fraction of HU protein. After the process through three kinds of column chromatographies, only the HU protein solution, which could be checked by SDS polyacrylamide gel electrophoresis, was obtained. Finally we lyophilized the solution and obtained about 60 (milli-gram) in powder of HU protein.

b) **preparation of DNA**: We synthesized two kinds of complementary single stranded DNA of 20mer (20 bases long) [Fig.3]. The DNA base sequence was designed so that DNA-binding proteins should bind easily in the central A-T rich region and the DNA be stabilized by G-C pairs at the both ends. The crude product of DNA was purified, and the pure solution lyophilized to get double stranded DNA of 20b.p. (base pair) long by annealing the mixed solution of two kinds of single stranded DNA.

\[
\text{5'}-\text{GCACAACTAAATGCATAACG-3'} \\
\text{3'}-\text{CGTGTTGATTAACGTATGC-5'}
\]

*Fig. 3*: The base paired sequence of complementary DNA synthesized. The two types of base pairing (hydrogen bonding) are permitted, between A (adenine) and T (thymine), and between G (guanine) and C (cytosine).

c) **instruments**: The small angle X-ray (SAXS) and neutron (SANS) scattering experiments were executed at BL10c of Photon Factory in KEK and at SANS-U of JRR-3M in JAERI respectively. The optical conditions of each instrument were selected as to cover low Q region enough to be able to observe 40 (Angstrom) Rg in the Guinier region.

d) **Rg calculation from models**: The crystal structure data for Rg calculation from the model were obtained from PDB; Protein Data Bank. The contribution of hydrogen atoms was not included in the calculation. For the volume integration in the Rg calculation, the molecule was cut with the unit volume of cube, 2\textsuperscript{3} (Angstrom\textsuperscript{3}).

e) **experimental conditions**: All experiments were carried out near at the room temperature and the pH of sample solutions was about 7 with proper buffers.
RESULTS & DISCUSSION

a) HU protein: SAXS results from the HU protein solution are shown in Fig.4. When the concentration of HU protein decreases and is extrapolated to zero, $R_g$ becomes 19 (Angstrom). $R_g$ was calculated from the crystal structure (dimer) data, and was 17.8 (Angstrom). In this calculation, some undetermined portion in the arms was not included, and when this portion is created by the computer graphics and added in the $R_g$ calculation, it was obtained as 20.1 (Angstrom). These results show that HU protein exists as a dimer in solution and that the portion of arm regions invisible in the X-ray crystallography might be detected in the solution scattering.

![HU protein alone by SAXS](image1)

**Fig. 4(left):** Guinier plot of HU protein by SAXS, the $R_g$ increases as the concentration decreases.

**Fig. 5(right):** 20b.p. DNA by SAXS.

$Q = 4\pi\sin\theta/\lambda$, $2\theta$: scattering angle, $\lambda$: wave length.

b) 20b.p. DNA: SAXS results from the 20b.p. DNA in solution are shown in Fig.5. In the case of DNA the experimental measured $R_g$ was obtained as 20.2 (Angstrom) and this is in good agreement with the calculated one; 21 (Angstrom).

c) HU-DNA complex: In the SANS and SAXS experiments, three experimental parameters were selected in the HU-DNA complex solution, those are, the molar ratio (Mr) (= [HU protein dimer]/[DNA 20bp] ), the salt concentration ([NaCl]) and the total concentration (= [HU protein dimer]+[DNA20bp] ) in order to deduce the structural information of HU-DNA complex coordinately for stoichiometry, for effects of electrostatic-shielding of ions and for solute concentration effects.

★ [NaCl]=50mM

Guinier plots from SANS & SAXS experimental results are shown in Fig.6 & 7 respectively. Obtained $R_g$ were scattered from 32 to 35 (Angstrom). In order to explain these $R_g$ values, we have proposed the complex model of HU protein dimer and 20b.p. DNA, and the model was created by the computer graphics. After many trials on the models, we have been able
to give one model[Fig.8] which explains the observed Rg values very well, and the model indicates that HU protein of dimer might bend DNA in a cell.

**Fig.6(left)**: Guinier plot of HU-DNA complex by SANS, molecular ratio(Mr) is 1.0.

**Fig.7(right):** By SAXS, molecular ratio(Mr) is 2.08.

**Fig.8(below):** Two tetramer complexes contacted at an angle of 210 degrees. HU protein is represented by α-carbon atoms of each amino acid, and DNA by phosphate back bone atoms.

All experiments under the [NaCl]=50mM condition are summarized in Fig.9. We can see two things in this figure. One is that the Rg values increase as the molar ratios become high. The model that several forms of HU-DNA complexes coexist in equiribrium[Fig.10] can account for this tendency. Another one is that the Rg values increase as the total concentration becomes large. This indicates there is some cooperative binding of HU protein to DNA. For further discussion, additional experiment and analysis might be required, however, these findings are very important from the standpoint of gene operating system of nonspecific DNA-binding proteins.
**Fig. 9:** Summarized Rg under high salt concentration of [NaCl]=50mM. To understand the relation between Mr and Rg, complex equilibrium model system as Fig.10 is required. Another Rg behavior of rising as total concentration indicates that there might be some cooperative binding between HU protein and DNA.

\[ \text{Mr = [HU dimer] / [DNA]} \]

**Fig. 10:** Equilibrium model of HU-DNA complexes. Mw is molecular weight in kDa (1000 atomic weight) unit, and Rg is radius of gyration (Angstrom). It is thought that the variation of 'Rg = 34.2' complex particle ratio affects the observed Rg values. Each equilibrium constant has not been ever determined.
Fig. 11 shows the convolution between the structure factor and the first peak of Laue diffraction in the Q-I(Q) plot by SANS. Such a curve can be observed in the diffraction from the liquid because the interparticle interaction causes the solution to be no longer ideal dilute. The sample solution is the mixture of HU protein dimer and DNA 20b.p. in the same number of molecule. As the total concentration becomes larger, the first Laue peak shifts to higher Q, that is, the nearest neighbor distance of HU-DNA complex particles in real space becomes smaller. This tendency, especially observed in [NaCl]=10mM not in [NaCl]=50mM, is more prominent than in the case of HU protein alone or DNA alone. Such a phenomenon had been recognized in the case of eucaryotic histone and DNA complex (nucleosome) at the low salt concentration).

Fig. 11: Interparticle effect of HU protein and DNA mixed system by SANS. As the total concentration increases, the peak position shifts to higher Q. This is a liquid behavior in the cause of strong interaction between complex particles.

REFERENCES

SMALL ANGLE NEUTRON SCATTERING STUDY OF THE INITIAL STAGE OF LYSOZYME CRYSTALLIZATION PROCESS.

*1Yoshiaki MINEZAKI, *1Ichiro TANAKA, *1Nobuo NIIMURA, *2Mituo ATAKA, and *2Tatsuo KATSURA

*1Laboratory of Nuclear Science, Tohoku University
Mikamine, Taihaku-ku, Sendai-city, Miyagi-ken, 982 Japan

*2 National Institute of Bioscience and Human-technology
Higashi, Tsukuba-city, Ibaraki-ken, 305 Japan

ABSTRACT

Despite the enormous amount of information obtained from atomic resolution crystal data, the difficulties encountered in growing crystals preclude structural X-ray studies for the majority of known isolated proteins. The protein crystal growth process can be studied by electron microscopy and by light scattering, and recently Ataka & Asai\(^1\) have discussed the kinetics on lysozyme crystal growth.

We have conducted small angle neutron scattering (SANS) experiments on the time evolution from the initial stages to the visible size of crystallization of hen egg-white lysozyme. SANS from several kinds of solutions have been carried out. The SANS result showed the distinctive change of time evolution.

We have also conducted the experiments under various unsaturated conditions using SANS. From these experiments, we found that even under unsaturated conditions, aggregation of lysozyme was found to be started, against the result of light-scattering experiments.

INTRODUCTION

On the molecular biology, the determination of the three-dimensional structures of biological macromolecules, i.e. proteins, nucleic acids, etc. is the key to elucidate the mystery of life. Among the three major techniques, X-ray crystallography, nuclear magnetic resonance, and electron microscopy or electron diffraction (and very recently, also neutron crystallography),
crystallography has been the main and the most powerful tool for this purpose. In the field of the crystallography, many progresses in techniques, sources, etc. have been developed during the last decade. But even now, the crystallization process is the most mysterious and unknown, and the bottleneck for crystallography. Recently the work to know it has started all over the world using many methods. We have also started to know the early stage of crystallization process of lysozyme using SANS methods.

EXPERIMENTAL

We have carried out SANS experiments using two kinds of instruments. One is the SANS-U located at the C1-2 beam port of the JRR-3M of JAERI. Incident neutron wavelength is 7.0A. And sample-to-detector distance is 4000 mm to cover the Q-range between 0.005 Å⁻¹ and 0.1 Å⁻¹, and also used 12000 mm to cover the Q-range between 0.002 Å⁻¹ and 0.03 Å⁻¹. The other is WIT at KENS in Tukuba. The covered Q-range used for this experiment is between 0.055 Å⁻¹ to 0.144Å⁻¹.

Lysozyme was purchased from Seikagaku Kogyo Coop.

The time-evolution of the crystallization has been observed in a quartz sample cell (4mm in thick) in D2O buffer at every 30 minutes for two days. The lysozyme concentration is 4.0 wt%, the one of NaCl is 3.0 wt%, pH is 4.7, and the temperature is 18 °C. Under this condition the crystal grows for two days. As a reference, the unsaturated conditions, such as the NaCl concentration is 1.5 wt% and others are the same as before, are adapted. Under this condition, the crystal never grows. And we have also observed another condition under which crystal grows for one day.

The effect of NaCl to the crystallization process has been studied by changing the NaCl concentration in the solution from 0 wt% to 3.0 wt%, under the concentration of which the lysozyme solution becomes supersaturated. Lysozyme concentration is 20 mg/ml, pH is 4.6, temperature is 18 °C, and NaCl concentration is selected as 0, 0.12, 0.3, 0.6, 1.2, 1.8, 2.4 and 3.0 wt%.
RESULTS

(1) Time-evolution of crystal growth

Under the undersaturated conditions, crystal never grows and no change in SANS was observed. On the other hand, the drastic change was seen under supersaturated conditions. Fig.1 shows the time dependence of all the scattered neutrons detected on the total area of the detectors. Closed-circles are the result under the saturated condition where crystal grows, and closed-squares are the one under the unsaturated condition where crystal doesn't grow. Fig.2 shows the time-evolution of I(q) which is obtained under the saturated condition. I(q)'s at the first 30 minutes in every two hours are displayed on this graph. Fig. 2 indicates that I(q) changes dramatically as the time elapses.

We have tried to carry out the Guinier plot and to extract I(0), the extrapolation value to Q=0, and the apparent radius of gyration Rg though the system is multi-dispersive. Fig.3 and Fig.4 show the time evolution of I(0), and of Rg, in the q region of 0.004 Å⁻²<q²<0.019 Å⁻¹, respectively. Fig.3 and Fig.4 indicate that as far as the q-range considered, the number and the size of aggregated lysozyme clusters might be gradually changed.
(2) Change of NaCl concentration

Fig. 5 shows the change of I(q) with the various NaCl concentrations in D₂O. As the NaCl concentration increases, I(q) increases gradually and the peak shifts toward the low-Q region. The peak appears because of the interaction between the particles and the peak position reflects the distance between the particle: the fact that the peak shifts toward the low-Q region means that interparticle distances become long. Since the concentration of lysozyme is constant in this measurement, this phenomenon might be explained as lysozyme molecules aggregate when NaCl is added, and the more NaCl concentration increases, the more the aggregation occurs. This fact is very interesting and important to understand the lysozyme crystallization process.
DISCUSSION

The effort to know the crystallization process of protein has been just started at everywhere since only a few years ago by using several methods. Direct observation of the crystallization process in the microscopic level is very important, and for that purpose the SANS experiment might be superior to other method, especially the small angle X-ray scattering (SAXS) experiment. The reasons are as follows: (1) It takes one day or so to complete the protein crystallization, and if X-ray is used, radiation damage might occur during the measurement for one day. (2) The sample thickness is less than 1mm for the SAXS, and the surface effect of the cell cannot be neglected. (3) The addition of the salt such as NaCl is necessary for the protein crystallization, and this affects the absorption of X-rays fatally.

We have started the preliminary observation of the initial stage of the crystallization process of lysozyme by using the SANS experiment. Fortunately we could get two results as follows; (1) We could follow early stage of lysozyme crystallization process, and (2) we could discover that the transition from the unsaturated state to the saturated one might look like continuous, and even under the unsaturated condition the aggregation of lysozyme might occur.

We could not put the clear line between our results of I(q) under the saturated or unsaturated states. We must have an important question. What is the difference between the saturated and unsaturated states in the microscopic level? The answer will give us the solution to understand the microscopic mechanism of the crystallization process.

REFERENCE

1) M. Ataka & M. Asai; Biophys. J. 58 (1990) 807–811
PHASE TRANSITIONS AND STRUCTURES OF METHYLAMMONIUM COMPOUNDS

*Osamu YAMAMURO, *Noriko ONODA-YAMAMURO, *Takasuke MATSUO, *Hiroshi SUGA, **Takashi KAMIYAMA, **Hajime ASANO, **Richard M. IBBERSON, and ***William I.F. DAVID

*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

**Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

***ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England

ABSTRACT

The structures of $\text{CD}_3\text{ND}_2\text{Cl}$, $\text{CD}_3\text{ND}_2\text{I}$, $\text{CD}_3\text{ND}_2\text{BF}_4$, ($\text{CD}_3\text{ND}_2$)$_2\text{SnCl}_6$, and $\text{CD}_3\text{ND}_2\text{SnBr}_3$ crystals were studied with time-of-flight type high-resolution powder diffractometers using spallation pulsed neutron sources. The orientations of the $\text{CD}_3\text{ND}_2$ cations, including the positions of the D atoms, were determined at all the room temperature phases and at the low temperature phases of $\text{CD}_3\text{ND}_2\text{I}$ and ($\text{CD}_3\text{ND}_2$)$_2\text{SnCl}_6$. The heat capacity experiments were also performed for both protonated and deuterated analogs of these compounds. From both structural and thermodynamic points of view, it was found that the transitions are mainly associated with the order-disorder change of the orientations of the $\text{CD}_3\text{ND}_2$ cations.

INTRODUCTION

Methylammonium (MA) ion $\text{CH}_3\text{NH}_3^+$ forms NaCl, CsCl, anti-fluorite, and perovskite type crystals with various halogens and anion groups. These substances can be regarded as hybrid between ionic and molecular crystals since both van der Waals interaction of CH$_3$ and ionic one of NH$_3^+$ are important. Another interesting aspect is the rotational motions of MA$^+$ ion which has $C_3$ symmetry and two types of rotational modes; i.e. around the C-N axis and the C-N axis itself. These properties cause interesting transition phenomena in most of the MA compounds. In comparison with numerous experimental and theoretical works on ammonium compounds, however, there have not been sufficient studies on the phase transitions of these compounds, especially for their structural changes. The structural study is scarce because the transitions are mostly associated with the order-disorder of protons and are of first order, both making the X-ray diffraction study difficult.

Recently, the neutron powder diffraction technique has made a great progress in its capability and is now widely applied to the studies on various phase transitions. We have made neutron powder diffraction experiments on the deuterated analogs of MACl$^{11}$, MAI$^{12}$, MABF$_4$$^{13}$, MA$_2$SnCl$_6$$^{14}$, and MASnBr$_3$$^{15}$ crystals. In advance of the neutron experiments, the heat capacities of both protonated and deuterated analogs of these compounds were measured in the temperature range 13-300 K$^{11,12,13,14,15}$. In this paper, we concentrate mainly on the structure of the disordered phases and discuss the nature of the phase transitions from both
structural and thermodynamic points of view.

EXPERIMENTAL

The neutron diffraction experiments were performed with two high-resolution powder diffractometers at KENS (HRP)\(^{12}\) and ISIS (HRPD)\(^{13}\). MACI, MABF\(_4\), and MASNBr\(_3\) were measured with HRP and MAI and MA\(_2\)SnCl\(_6\) with HRPD. Both of the instruments are time-of-flight (TOF) type using the spallation pulsed neutron sources. The powder samples of about 5 cm\(^3\) were contained in a vacuum-tight cylindrical can made of vanadium. The observed TOF ranges are 5-32 ms, corresponding to the d-spacing of 0.5-3.2 Å, for the former and 30-280 ms, corresponding to 0.6-5.6 Å for the latter apparatus. The resolutions (\(\Delta d/d\)) were 0.3 % and 0.08 %, respectively. The data were collected at each phases in the temperature range 5-300 K.

The heat capacity experiments were carried out with low temperature adiabatic calorimeters\(^{14,15}\) at Osaka. The sample mass used was about 2 g for all of the calorimetric experiments. The observed temperature range was 13-300 K and the accuracy of the measurement was 0.1 % above 30 K.

The CH\(_3\)NH\(_3\)I and CH\(_3\)NH\(_3\)BF\(_4\) crystals were synthesized by dissolving CH\(_3\)NH\(_2\) gas into HI and HBF\(_4\) aqueous solutions, respectively. The CH\(_3\)NH\(_2\) gas was produced by mixing CH\(_3\)NH\(_3\)Cl and NaOH in aqueous solution. (CH\(_3\)NH\(_2\))\(_2\)SnCl\(_6\) was prepared from CH\(_3\)NH\(_3\)Cl and SnCl\(_6\) and CH\(_3\)NH\(_3\)SnBr\(_3\) by mixing CH\(_3\)NH\(_3\)Br\(_2\) and SnBr\(_3\) in ethanol. All the crystals were purified by recrystallizing from ethanol several times. Fully deuterated analogs of these compounds were prepared by the same procedure using CD\(_3\)NH\(_2\) as starting material and recrystallizing from heavy water in strict exclusion of atmospheric moisture. The purity of these substances were checked by elemental analyses. The deuteration ratio was confirmed to be more than 99 % for all of the deuterated substances.

RESULTS AND DISCUSSION

Heat Capacity and Phase Transitions

Figure 1 shows the heat capacity curves of both protonated (solid circles) and deuterated (open circles) MAI crystals\(^2\). A lambda type transition between \(\alpha'\) and \(\delta\) phases was observed in both samples. A lambda transition of MA\(_2\)SnCl\(_6\) was much sharper and described as a critical phenomenon. Figure 2 shows the transitional heat capacity of the deuterated
MA$_2$SnCl$_6$. The critical exponent $\alpha(T>T_s)$ determined by the least-squares fitting of the excess heat capacity was 0.65 and $\alpha'(T<T_s)$ 0.24. Likewise, the heat capacity measurements of other MA compounds revealed that they have one or more phase transitions below room temperature. Table 1 summarizes the temperature and entropy of the phase transitions. The symbols F and H in the parentheses after the transition temperatures denote the order of the transitions (F: first order, H: higher order).

It is noteworthy that most of the phase transitions exhibit transition entropy larger than $R \ln 2$. This indicates that the transitions are of order-disorder type. It was also found that the isotope effect on the transition is small enough to be neglected in the discussion of the mechanisms of the phase transitions.

Table 1. Thermodynamic quantities associated with the phase transitions of various methylammonium compounds.

<table>
<thead>
<tr>
<th>H compounds</th>
<th>D compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{trs}$/K</td>
</tr>
<tr>
<td>MACl</td>
<td>220.4 (F)</td>
</tr>
<tr>
<td>MAI</td>
<td>264.5 (F)</td>
</tr>
<tr>
<td>MABF$_4$</td>
<td>156.1 (H)</td>
</tr>
<tr>
<td>MA$_2$SnCl$_6$</td>
<td>251.3 (F)</td>
</tr>
<tr>
<td>MA$\text{SnBr}_3$</td>
<td>154.3 (H)</td>
</tr>
<tr>
<td></td>
<td>46.0 (F)</td>
</tr>
<tr>
<td></td>
<td>188.2 (F)</td>
</tr>
<tr>
<td></td>
<td>213.0 (H)</td>
</tr>
<tr>
<td></td>
<td>229.4 (F)</td>
</tr>
</tbody>
</table>

Structures of MAX (X=Cl, I, BF$_4$)

The crystal structures of the room temperature phases of MACl (\(\alpha\)) and MAI (\(\alpha'\)) have been studied by single crystal X-ray diffraction\(^{(6)}\) and the positions of the C, N, and halogen atoms were determined as shown in Fig. 3. The former corresponds to the CsCl type and the latter NaCl type. Both of these structures belong to the P4/nmm space group and the C-N axes of the MA$^+$ ions coincide with the crystallographic four-fold axes. It is also known that MABr exhibits the $\alpha'$ phase at room temperature and the $\alpha$ phase above 385 K\(^{(18)}\). The positions of the D atoms have not been determined. It is likely that MA$^+$ ions have to be orientationally disordered in accord with the crystallographic symmetry and the transitions are due to their ordering. The $\delta$ phase of MAI should belong to subgroup of P4/nmm in view of the higher order nature of the $\delta$-$\alpha'$ phase transition.

Among the three phases ($\alpha$, $\beta$ and $\gamma$) of the deuterated MACl, the room temperature $\alpha$ phase has been studied in the present investigation\(^{(4)}\); complete data of the $\beta$ and $\gamma$ phases have not been collected. The diffraction pattern of the $\alpha$ phase is shown in Fig. 4. By using the X-ray data\(^{(6)}\) as the initial values, the structural parameters, including

![Fig. 3. Structures of the $\alpha$ and $\alpha'$ phases of MAX determined by X-ray diffraction.](image-url)
those of the D atoms, were refined by the standard Rietveld method\(^9,20\). The observed intensities are represented by plus symbols and those calculated for the final structure model by a solid curve. The expected peak positions and the deviations are also given below them. Excellent fit was attained over the whole d-spacing range \(R_{wp}=3.70\%\), \(R_{exp}=2.43\%\). The present analysis revealed that the MA\(^+\) ion has four-fold orientational disorder around the C-N axis. For each orientation of the MA\(^+\) ion, one of the three D atoms of the ND\(_3\) group is located on the mirror plane and pointing to one of the Cl\(^-\) ions sitting at the eight corners of the tetragonal primitive cell. Figure 5 shows the Fourier contour map \((F_{obs})\) in the a-b plane at \(z=0.88\) level where the D atoms of ND\(_3\) group are located. The four-fold disorder of the MA\(^+\) ion is indicated for the sake of clarity by the four symbols (circles, triangles, squares, multiples). This result is consistent with the transition entropy of the \(\gamma-\alpha\) transition \((=R \ln 4)\) and suggests the existence of weak N-H...Cl hydrogen bonds.

The neutron diffraction data of MAI were collected at room temperature (\(\alpha\) phase) and 5 K (\(\delta\) phase)\(^2\). Unlike the \(\alpha\) phase of MACI, the positions of the D atoms could not be determined in the \(\alpha\) phase because of their large temperature factors. This result suggests that the D atoms do not jump between distinct equivalent positions but are rotating almost freely around the C-N axis. The difference between the \(\alpha\) and \(\alpha\)\(^+\) phases may be related to the structural peculiarity of the \(\alpha\) phase in which the ND\(_3\)\(^+\) group has no halide ions in its immediate environment to make hydrogen bonding with.

Figure 6 shows the diffraction pattern of the \(\delta\) phase: the observed and calculated intensities are shown by dots and a solid curve, respectively. The structure of the \(\delta\) phase was determined by the Rietveld analysis \((R_{wp}=3.33\%, R_{exp}=1.22\%)\). The determined structure \((Pbma, Z=4, a=7.1743, b=7.0967, c=8.8323\text{\ Å})\) is illustrated in Fig. 7\(^2\). It was found that the \(\alpha\) lattice becomes distorted along the \(<110>\) direction through the transition and the new a and b axes of the \(\delta\) phase are related to \(\sqrt{2}\) times of the tetragonal a axis. The orientation of the MA\(^+\) ions is ordered in an anti-parallel way. This result is consistent with the calorimetric
one; i.e., the transition is of order-disorder type and of higher order nature.

The structure of the room temperature phase of MABF$_4$ was recently determined in a single crystal X-ray study$^{23}$. This structure is similar to the $\alpha'$ phase, where the orientation of the BF$_4$ ion is additionally highly disordered. The neutron powder diffraction was performed at room temperature to determine the D atom positions$^{23}$. However, the distinct positions of the D atoms of the MA$^+$ ion could not be found as in the case of MAI.

Structure of MA$_2$SnCl$_6$

From the single crystal X-ray study$^{22}$, both of the room temperature and low temperature phases have been reported to belong to the same space group R3m though the H atoms were not located. Considering the large transition entropy, the transition was likely to be an order-disorder change of the H atom positions of the MA$^+$ ion, in spite of the reported identical space groups.

Figure 8 schematically shows the structure of MA$_2$SnCl$_6$ determined by X-ray. This structure is basically an anti-fluorite type and the cubic-to-rhombohedral distortion is shown by an arrow. The MA$^+$ cation is located at the center of the distorted tetrahedron formed by the octahedral SnCl$_6$ groups and the C-N axis coincides with the crystallographic three-fold axis. It is noteworthy that the CH$_3$ group is surrounded by the three Cl atoms and the NH$_3$ group by the nine Cl atoms.

The neutron diffraction data were collected at 300 K and 5 K$^9$. The high temperature data were analyzed based on the structure determined by X-ray (R3m). The model in which the D atoms are distributed over two sites placed symmetrically on either side of the mirror plane provided the best convergence of the refinement ($R_{wp}$=6.7 % $R_{exp}$=7.4 %). The diffraction pattern of the low temperature structure contained a number of extra peaks which suggest a reduced symmetry. The refinement based on the R3 space group converged satisfactorily.

---

Fig. 6 Neutron diffraction pattern of δ MAI observed by HRPD.

Fig. 7 SCHAKAL$^{21}$ illustration of δ MAI.
with $R_{exp}=4.9\%$ ($R_{exp}=2.9\%$). In Fig. 9, the Fourier maps ($F_{calc}$) of the sections including the D atoms of the $\text{ND}_3$ and $\text{CD}_3$ groups at $300\text{ K}$ and $5\text{ K}$ are drawn. It is clearly shown that the two-fold disorder of the $\text{MA}^+$ cation is lifted through the transition. The two equivalent orientations of the $\text{MA}^+$ ion in the high temperature phase may be a result of the electrostatic interactions between the D atoms of the $\text{ND}_3^+$ group and the negative-charged Cl atoms of the $\text{SnCl}_6^{2-}$ ion. It is also worth noting that the R3m-R3 change satisfies the group-subgroup relationship for a higher order phase transition. In addition it is a change within the same (rhombohedral) crystal system. The latter property of this phase transition explains an exceptionally strong divergence of the heat capacity anomaly as a consequence of a very short effective range of interaction in this compound.

**Structure of $\text{MASnBr}_3$**

$\text{MASnBr}_3$ exhibits the most complicated phase behavior of the MA compounds studied\(^1\). It is known from the X-ray powder diffraction\(^2\) that the room temperature phase crystallizes in the cubic perovskite structure as shown in Fig. 10. The orientation of the $\text{MA}^+$ ion is expected to be highly disordered to satisfy the site symmetry of $\text{m3m}$.

The neutron diffraction experiment was performed at room temperature\(^5\). To determine the orientations of the C-N axis, we have tested three models in which the C-N axis coincides with the crystallographic four-fold axis (model A), the two-fold axis (model B), or the three-fold axis (model C). These models are schematically shown in Fig. 11, where the arrows denote the equivalent directions of the N atom of the centered $\text{MA}^+$ ion. The model in which the $\text{MA}^+$ ion was approximated to be a sphere at the $(1/2,1/2,1/2)$ position was also tested (model D). The Rietveld refinements were carried out for these models in which the adjustable parameters were the magnitude of displacement of the $\text{MA}^+$ ion along the direction of the C-N axis (except the model D) and the isotropic temperature factors. The final $R_{wp}$ value were as follows; model A: 2.88\%, B: 2.48\%, C: 3.03\%, D: 9.34\% (R$_{wp}$=2.76\%). No significant improvement in $R_{wp}$ was obtained for further test considering the orientations along the C-N axis. The
model B gave the smallest $R_{wp}$. However, it should be noted that the models A and C also gave comparable magnitudes of $R_{wp}$. It is concluded that the orientation of the C-N axis distributes over various orientations including A, B, C and the most preferred one is that of the model B. This result is quite consistent with the large value of the total transition entropy (28.9 JK$^{-1}$mol$^{-1}$).

CONCLUDING REMARKS

It was found that the phase transitions of the studied MA compounds are associated with the orientational disorder of the hydrogen (deuteron) atoms around the C-N axis and the C-N axis itself. The preferred orientations of the MA$^+$ ion in the disordered phase were dominated by the site symmetry of the MA$^+$ ion and the electrostatic and/or hydrogen-bonding interaction between the NH$_3$ group and the halogen ions. The neutron diffraction technique combined with the calorimetric experiment is a very powerful approach to investigate this type of phase transition problems.

ACKNOWLEDGMENTS

The authors in Osaka University gratefully acknowledge Professor Noboru Watanabe for his kind leading to the neutron diffraction work in KEK. They are also indebted to Dr. Fujio Izumi for his useful advice on the Rietveld-analysis program RIETAN, and Dr. Tooru Ishigaki, Mr. Hiroyuki Baba, Mr. Izumi Ohta, and other students in Asano Laboratory, University of Tsukuba for their great help in the neutron diffraction experiments on HRP. The authors in Osaka University and RAL acknowledge the British Council for the financial support of this collaboration.

REFERENCES

8) N. Onoda-Yamamuro, O. Yamamuro and H. Suga, to be published.
17) S.B. Hendricks, Z. Kristallogr. 67, 106 (1928).
21) E. Keller, SCHAKAL, A Fortran Program for the Graphical Representation of Molecular and Crystallographic Models. Albert-Ludwigs-Univ. Freiburg, Germany.
STRUCTURE AND DYNAMICS OF AQUEOUS ELECTROLYTE SOLUTIONS BY NEUTRON SCATTERING

Toshio YAMAGUCHI,* Motoyuki YAMAGAMI, Toshiyuki TAKAMUKU†, and Hisanobu WAKITA

Department of Chemistry, Faculty of Science
Fukuoka University
Nanakuma, Jonan-ku, Fukuoka 814-01 Japan

†Aqua Laboratory
Research and Development Division, TOTO Ltd.
Nakashima, Kokura-ku, Kitakyushu 802 Japan

ABSTRACT

Neutron isotopic substitution measurements have been performed in a temperature range of 90 - 474 K on a concentrated D₂O solution of lithium chloride using ⁷Li, ⁶Li (mixture of ⁶Li and ⁷Li), ³⁵Cl, and ³⁷Cl. The radial distribution functions obtained have revealed temperature dependent hydration structures of Li⁺ and Cl⁻. The isomorphous substitution technique has been successfully applied to aqueous perchlorate solutions of Pr³⁺-Nd³⁺, Tb³⁺-Dy³⁺, and Tm³⁺-Yb³⁺; the results have demonstrated a detailed coordination geometry of water molecules around the lanthanide(III) ions and a change in hydration number in the lanthanide series. The dynamic properties of water molecules in concentrated aqueous solutions of lithium chloride and zinc(II) bromide have been investigated at ambient temperature and in the supercooled state, the neutron quasi-elastic scattering method. The self-diffusion coefficients of water molecules are determined and discussed on the basis of the jump-diffusion model. The results from the neutron scattering methods are compared with those obtained from comparative X-ray diffraction, pulsed field gradient, nuclear magnetic relaxation measurements.

INTRODUCTION

The investigation of structure and dynamic properties of aqueous electrolyte solutions at the atomic scale is essential for understanding the physico-chemical properties and reactions taking place in the solutions. Among various techniques so far employed, the neutron scattering method is well suited to this purpose since the energy of neutrons can be varied from that of the motion of ions and water molecules in the solutions to that of neutrons used for diffraction. In addition, the scattering lengths of atoms do not depend of atomic number and are characteristic of the atoms; thus the information of light atoms like H, D, Li, etc., which is difficult to obtain by the methods using X-rays, is available by neutron diffraction. This implies, however, that a total neutron
diffraction study of aqueous electrolyte solutions suffers from elucidating the ion-solvent interactions because of predominant contribution from solvent-solvent interactions in the solutions. An isotopic/isomorphous substitution technique overcomes this difficulty and has been successfully used to determine the detailed structure of ionic hydration in aqueous electrolyte solutions. 1)

In the present study this technique has been employed to reveal temperature dependent hydration structure of Li\(^+\) and Cl\(^-\) in concentrated aqueous solutions of LiCl in D\(_2\)O in a wide range of temperature and the change in hydration number for a series of lanthanide(III) ions in aqueous perchlorate solutions. The neutron quasi-elastic scattering method has been used to investigate the dynamic properties of water molecules in aqueous solutions of zinc(II) bromide and lithium chloride from room temperature down to glassy transition temperature.

THE METHOD OF ISOTOPIC/ISOMORPHIC SUBSTITUTION

In the case of an aqueous electrolyte solution MX\(_n\).D\(_2\)O, the neutron scattering experiment gives us the total structure factor \(S(Q)\) consisting of ten partial structure factors \(s_{ij}(Q)\) related to the ion-water (M-O, M-D, X-O, X-D), ion-ion (M-M, M-X, X-X), and water-water (O-O, O-D, D-D) interactions,

\[
S(Q) = (\Sigma c_i b_i)^{-2} \Sigma \Sigma c_i c_j b_i b_j (s_{ij}(Q) - 1)
\]

where \(c_i\) is the atomic fraction, \(b_i\) the scattering length of the \(i\)-th particle, and \(Q\) the momentum transfer. When two scattering experiments are made on the aqueous solutions of the same compositions with isotopically/isomorphically different ions M, the difference function \(\Delta_M(Q)\) obtained from the two \(S(Q)\)s is given by

\[
\Delta_M(Q) = A(s_{MO}(Q) - 1) + B(s_{MD}(Q) - 1) + C(s_{MX}(Q) - 1) + D(s_{MM}(Q) - 1)
\]

\[
A = 2c_M c_0 b_0 (b_M - b_M'), B = 2c_M c_D b_D (b_M - b_M'),
C = 2c_M c_X b_X (b_M - b_M'), D = c_M^2 (b_M^2 - b_M'^2)
\]

The difference function \(\Delta_M(Q)\) is Fourier transformed to give the radial distribution function \(G_M(r)\) represented by

\[
G_M(r) = A(g_{MO}(r) - 1) + B(g_{MD}(r) - 1) + C(g_{MX}(r) - 1) + D(g_{MM}(r) - 1)
\]

Similar difference function \(\Delta_X(Q)\) and \(G_X(r)\) related to X are also obtained for the solutions with isotopically substituted X.

Neutron scattering measurements have been made on HIT at National Laboratory for High Energy Physics, Japan and on LAD at Rutherford Appleton Laboratory, UK. The isotopic substitution for a pair of \(^7\)Li and \(^9\)Li and of \(^35\)Cl and \(^37\)Cl has been applied to a 9.3 molal aqueous solution of lithium chloride in D\(_2\)O. 2), 3) Figure 1 shows the \(G_{Li}(r)\) obtained for the Li\(^+\)-substituted solutions at various temperatures. The first two peaks represent Li-O and Li-D interactions respectively within the hydrated Li\(^+\) ions. The sharp peaks clearly demonstrate that water molecules are firmly bound to an Li\(^+\) ion. The area for the Li-O peak decreases gradually with lowering temperature, and a
broad peak appears at 3.0-5.0 Å. The Cl\(^-\)-related radial distribution functions \(G_{CI}(r)\) are shown in Fig. 2 for the solutions. The first predominant peak is ascribed to Cl-D(1) hydrogen bonds, while in the second peak are superimposed Cl-O and Cl-D(2) interactions due to Cl\(^-\) hydration. Apparently the Cl-D(1) peak becomes sharper with lowering temperature, showing reinforced Cl...D-O-D hydrogen bonds in the supercooled and glassy states. A Gaussian fitting procedure has been applied to both \(G(r)\)s to characterize the hydration structure of Li\(^+\) and Cl\(^-\) quantitatively. The finally obtained parameter values are summarized in Table 1.

| Table 1. Parameter values for Li\(^+\) and Cl\(^-\) hydration. |
|------------------------------|-------------------------------|-----------------|-------|
| \(T/K\) | \(r(\text{Li-O})/\AA\) | \(r(\text{Li-D1})/\AA\) | \(\text{CN}\) | \(\text{State}\) |
| Li\(^+\) | 298 | 2.02(5) | 2.51(5) | 3.8(5) | L |
| | 258 | 1.95(5) | 2.58(5) | 4.0(5) | SL |
| | 213 | 2.03(5) | 2.62(5) | 3.6(5) | SL |
| | 173 | 2.04(5) | 2.57(5) | 2.7(5) | SL |
| Cl\(^-\) | 470 | 2.31(1) | 4.5(1) | L |
| | 350 | 2.31(1) | 5.7(1) | L |
| | 295 | 2.29(1) | 5.8(1) | L |
| | 173 | 2.26(1) | 5.6(1) | SL |
| | 94 | 2.28(1) | 5.8(1) | G |

L=liquid, SL=supercooled liquid, G=glass

It is concluded from the neutron diffraction data that above room temperature Li\(^+\) is rigidly bound to about four water molecules, whereas water molecules are randomly
distributed around Cl\textsuperscript{−}. In contrast, in the supercooled and glassy solutions the rigid hydration shell of Li\textsuperscript{+} is partly collapsed, while the water molecules bound to Cl\textsuperscript{−} are arranged more regularly.

The isomorphic substitution measurements have been made on 2 molar aqueous perchlorate solutions of isomorphic lanthanide pairs: Pr\textsuperscript{3+} - Nd\textsuperscript{3+}, Tb\textsuperscript{3+} - Dy\textsuperscript{3+}, and Tm\textsuperscript{3+} - Yb\textsuperscript{3+} in D\textsubscript{2}O at room temperature.\textsuperscript{4} Figure 3 shows the radial distribution function $G_M(r)$ obtained for the solutions of Tm\textsuperscript{3+} and Yb\textsuperscript{3+}. The predominant first and second peak correspond to the M-O and M-D interactions respectively within the first hydration shell of the lanthanide(III) ions. The analysis of the radial distribution functions has given the structural parameter values for the lanthanide(III) hydration in Table 2, which are also compared with those obtained from neutron isotopic substitution, X-ray diffraction, and extended X-ray absorption fine structure (EXAFS) methods. As seen in Table 2, the M-O and M-D distances obtained for the present isomorphic pairs are of accuracy comparable with those included in the other methods. The present results indicate that the hydration number of the lanthanide(III) ions changes from ~10 for the light ions to ~8 for the heavy ions in the series. The tilt angles of bound water molecules around the lanthanide(III) ions fall within the $\theta$ range 10-20$^\circ$ in the series. The values for the trivalent lanthanide(III) ions are significantly smaller than those found for monovalent ions Ag\textsuperscript{+} (45$^\circ$) and Li\textsuperscript{+} (40-52$^\circ$), and for divalent ions Ni\textsuperscript{2+} (42$^\circ$) and Ca\textsuperscript{2+} (34-38$^\circ$) in aqueous solution. The significant decrease in the tilt angle from the mono- or divalent ions to the trivalent ions is ascribed to much larger metal-water electrostatic interactions for the trivalent ions.

![Figure 3](image.png)

**Fig. 3.** The $G_M(r)$ function obtained for a 2 molar aqueous perchlorate solutions of Tm\textsuperscript{3+} and Yb\textsuperscript{3+} at room temperature.

THE NEUTRON QUASI-ELASTIC SCATTERING

In a neutron scattering process of a single atom, the double differential cross-section can be separated into two contributions as

$$
\frac{d^2\sigma}{d\Omega dw} = \frac{(k/k_0)}{2} [\langle b^2 > - < b >^2] S^{inc}(Q, \omega) + < b >^2 S^{coh}(Q, \omega)]
$$

$$
Q = k_0 - k
$$

where $S^{coh}(Q, \omega)$ and $S^{inc}(Q, \omega)$ are the coherent and incoherent dynamical structure factors, respectively, $k_0$ and $k$ the magnitudes of wavevector before and after scatter-
Table 2. Parameter values for the lanthanide(III) hydration obtained from the neutron isomorphic substitution, together with those from other methods.

<table>
<thead>
<tr>
<th></th>
<th>r(M-O)/Å</th>
<th>r(M-D)/Å</th>
<th>CN</th>
<th>Tilt angle/°</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr³⁺/Nd³⁺</td>
<td>2.48</td>
<td>3.14</td>
<td>10±1</td>
<td>22</td>
<td>ND</td>
<td>this work</td>
</tr>
<tr>
<td>Pr³⁺</td>
<td>2.539</td>
<td>9.2</td>
<td>9.5</td>
<td>5</td>
<td>XD</td>
<td>5</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>2.48</td>
<td>3.13</td>
<td>8.5</td>
<td>25</td>
<td>ND</td>
<td>6</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>2.513</td>
<td></td>
<td>8.9</td>
<td></td>
<td>XD</td>
<td>5</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>2.51</td>
<td></td>
<td>9.5</td>
<td></td>
<td>EXAFS</td>
<td>7</td>
</tr>
<tr>
<td>Tb³⁺/Dy³⁺</td>
<td>2.39</td>
<td>3.08</td>
<td>9±1</td>
<td>10</td>
<td>ND</td>
<td>this work</td>
</tr>
<tr>
<td>Tb³⁺</td>
<td>2.409</td>
<td></td>
<td>8.2</td>
<td></td>
<td>XD</td>
<td>5</td>
</tr>
<tr>
<td>Tb³⁺</td>
<td>2.400</td>
<td></td>
<td>8.0</td>
<td></td>
<td>XD</td>
<td>8</td>
</tr>
<tr>
<td>Dy³⁺</td>
<td>2.37</td>
<td>3.04</td>
<td>7.4</td>
<td>19</td>
<td>ND</td>
<td>6</td>
</tr>
<tr>
<td>Dy³⁺</td>
<td>2.39</td>
<td>3.03</td>
<td>7.9</td>
<td>29</td>
<td>ND</td>
<td>9</td>
</tr>
<tr>
<td>Dy³⁺</td>
<td>2.396</td>
<td></td>
<td>7.9</td>
<td></td>
<td>XD</td>
<td>5</td>
</tr>
<tr>
<td>Tm³⁺/Yb³⁺</td>
<td>2.33</td>
<td>3.02</td>
<td>8±1</td>
<td>12</td>
<td>ND</td>
<td>this work</td>
</tr>
<tr>
<td>Tm³⁺</td>
<td>2.358</td>
<td></td>
<td>8.1</td>
<td></td>
<td>XD</td>
<td>5</td>
</tr>
<tr>
<td>Tm³⁺</td>
<td>2.33</td>
<td></td>
<td>8.0</td>
<td></td>
<td>EXAFS</td>
<td>7</td>
</tr>
<tr>
<td>Yb³⁺</td>
<td>2.32</td>
<td>2.98</td>
<td>7.8</td>
<td>24</td>
<td>ND</td>
<td>9</td>
</tr>
</tbody>
</table>

ND=neutron diffraction, XD=X-ray diffraction, EXAFS=extended X-ray absorption fine structure

ing, respectively. In the aqueous solutions the proton (¹H) has a very large incoherent scattering cross section; the observed differential scattering cross section eqn. (4) can be approximated to the incoherent dynamic structure factor through

\[
\frac{d^2\sigma}{d\Omega dw} = \langle k/k_0 \rangle \langle b^2 \rangle - \langle b \rangle^2 S_{inc}(Q,\omega)
\]  

(5)

In aqueous solutions, water molecules are involved in translational, rotational, and vibrational motions; thus the incoherent dynamical structure factor may be described as a convolution of the three terms as

\[
S_{inc}(Q,\omega) = S^t(Q,\omega) \ast S^r(Q,\omega) \ast S^v(Q,\omega)
\]  

(6)

Here, the scattering law for the translational motion is expressed by the Lorentzian function as

\[
S^t(Q,\omega) = (1/\pi)|D_H Q^2/(D_H^2 Q^4 + \omega^2)|
\]  

(7)

where \(D_H\) is the translational diffusion coefficient of the proton.

The neutron quasi-elastic scattering measurements have been made on concentrated aqueous solutions of lithium chloride and zinc(II) bromide from room temperature to glassy transition temperature of the systems. The neutron experiments have been performed on LAM-40 spectrometer at a pulsed neutron scattering facility (KENS) of National Laboratory for High Energy Physics, Japan. Figure 4 shows the neutron quasi-elastic scattering spectra at \(Q = 1.755 \text{ Å}^{-1}\) for an aqueous solution of ZnBr₂.10H₂O at different temperatures.

As is seen in Fig. 4, the peak width for the solution decreases with lowering temperature, indicating that the motion of water molecules in the solutions is gradually restricted.
Fig. 4. The NQES spectra for an aqueous solution of ZnBr$_2$.10H$_2$O at different temperatures. The dots are experimental values and the solid lines are theoretical curves obtained from the least-squares fits described in the text.

Fig. 5. The $Q^2$-dependence of HHWM of the narrow component $\Gamma_n$ for the solutions of ZnBr$_2$.10H$_2$O and LiCl.6H$_2$O. The straight lines are theoretical values based on the Fick law using the $D_H$ values from NMR in Table 3.
with temperature. The spectra have been analysed by a curve fitting method using the following model function,

\[ S(Q,\omega) = C \left( A_n/\pi \{ \Gamma_n/(\omega^2 + \Gamma^2) \} + (A_b/\pi \{ \Gamma_b/(\omega^2 + \Gamma^2) \} \right) \]

where \( C \) is a constant, \( \Gamma_i \) (i=n and b) a half-width at half maximum (HWHM) of a Lorentzian component, \( A_i \) the fraction of the corresponding components. The HWHM values of the narrow component (n) are plotted against \( Q^2 \) in Fig. 5. The \( \Gamma_n \) values were analysed on the basis of a jump diffusion model:

\[ \Gamma_n = D_H Q^2 /[1 + D_H Q^2 \tau_0] \]

where \( D_H \) is the proton self-diffusion coefficient, and \( \tau_0 \) is the life time of the proton oscillatory motion. The self-diffusion coefficient \( D_H \) can be expressed by the mean jump length of proton \( L \) and \( \tau_0 \) as

\[ D_H = \langle L^2 \rangle / (6 \tau_0) \]

The obtained parameter values are summarized in Table 3. The self-diffusion coefficient of the proton decreases for both solutions with lowering temperature, suggesting that the translational motion of water molecules is restricted with temperature. This is probably because of the water-water interaction will be enhanced with decreasing temperature. The self-diffusion coefficients obtained from the neutron scattering are less than those determined by the \(^1\)H NMR pulsed field gradient method. A probable reason for the difference in \( D_H \) is ascribed to low resolution (~200 \( \mu \)eV) of the LAM 40 spectrometer. The experiments with high resolution (~1 \( \mu \)eV at \( Q \ll 1 \text{ Å}^{-1} \)) will be required to obtain a more accurate self-diffusion coefficient of the water proton.

<table>
<thead>
<tr>
<th>R</th>
<th>T/K</th>
<th>( \tau_0 ) ps</th>
<th>( L ) Å</th>
<th>( D_H/10^{-10} \text{m}^2 \text{s}^{-1} )</th>
<th>( D_{H}^{\text{NMR}}/10^{-10} \text{m}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBr(_2).( H_2)O</td>
<td>5</td>
<td>295</td>
<td>11.05</td>
<td>1.74</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>295</td>
<td>6.6</td>
<td>1.05</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>263</td>
<td>19</td>
<td>1.20</td>
<td>1.24</td>
</tr>
<tr>
<td>LiCl</td>
<td>6</td>
<td>295</td>
<td>7.1</td>
<td>1.10</td>
<td>2.60 (53 K)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>267</td>
<td>17</td>
<td>1.16</td>
<td>1.33 (298 K)</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>267</td>
<td>17</td>
<td>1.16</td>
<td>1.74 (263 K)</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

The neutron isotopic/isomorphic substitution method is very powerful in elucidating the microscopic pictures of electrolyte solutions in terms of the interatomic distance, the coordination number, and the orientation of water molecule around ions. The neutron quasi- and inelastic scattering method also gives us useful information on the dynamic properties of the electrolyte solutions. Since intense pulsed neutron facilities are
in progress, neutron scattering studies on electrolyte solutions will have a bright future. Combination of neutron with X-ray scatterings using synchrotron radiation are the most effective in molecular approaches to structure and dynamics of liquids and solutions.

ACKNOWLEDGMENTS

The present works have been partially supported by a Grant-in-Aid for Scientific Research on Priority Area of "Molecular Approaches to Non-equilibrium Processes in Solutions" (No. 02245106, 03231105, 04215104) from the Ministry of Education, Science and Culture, Japan.

REFERENCES


ION DYNAMICS IN MOLTEN MELKALTAL NITRATES

*Takashi Kamiyama, *Kaoru Shibata, *Kenji Suzuki and *Yoshio Nakamura

*Faculty of Science
Hokkaido University
Kita 10 Nishi 8, Kita-ku, Sapporo-shi, Hokkai-do, 060 Japan

*Institute for Materials Research
Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai-shi, Miyagi-ken, 980 Japan

ABSTRACT

Quasielastic neutron scattering experiments have been performed on simple molten alkali metal nitrates, RbNO₃ and LiNO₃. The experiments were carried out by the medium resolution inverted geometry spectrometer LAM-40 at KENS neutron scattering facility in Japan. The measured spectra are composed of narrow and broad quasielastic spectra. We assigned that the broad component corresponds to the fast intra-ionic motions in a nitrate ion. From momentum dependence of integrated intensity for this component it is found that the motion of nitrate ions in RbNO₃ melt is mainly the librational one centered C₃ axis on the ion. On the other hand the intra-ionic motion in LiNO₃ is the librational motion centered C₃ axis on the nitrate ion which amplitude is smaller than in RbNO₃ melt. This fact shows that the motion of nitrate ions in LiNO₃ is restricted strongly by surrounding cations.

INTRODUCTION

Quasielastic neutron scattering is a unique technique for the study of the diffusive motions for molecules. It provides both dynamical and geometrical information. The geometrical information is mainly included in coherent scattering, but little studies have been reported about coherent quasielastic neutron scattering. In this study we measured the quasielastic scattering for molten RbNO₃ and LiNO₃. In them neutrons are almost completely coherently scattered by a nitrate ion¹). We analyzed the coherent quasielastic neutron scattering data for evaluating the intra-ionic diffusive motion of a polyatomic nitrate ion in molten salts.

In alkali metal nitrate systems only nitrate ions have intra-molecular structure. So intra-molecular motions like molecular rotation are restricted to them within the nitrate ions. The
rotational motions of molecules depend on nonspherical steep repulsive force from their neighboring ions in ionic liquids. Then the difference of microscopic surroundings around the nitrate ion appears in its intra-molecular motions. From this point of view we have chosen simple alkali metal nitrates, RbNO₃ and LiNO₃, because of the difference of their cation size between them.

EXPERIMENTAL

Commercial RbNO₃ powder (Soekawa Chemicals, Tokyo; 99%) was used in this study. Isotopically enriched ⁷LiNO₃ was prepared from ⁷LiOH (98.2 atomic% ⁷Li enriched) and commercial aqueous HNO₃. They were handled in vacuum or dry Ar gas atmosphere because of their hygroscopic natures. After drying in vacuum at 100 to 150 °C for one day, the powders were sealed into aluminum metal double cylindrical containers for neutron scattering experiments under a dry Ar gas atmosphere. The container was of 14 mm in outer diameter, 8 mm in inner diameter and 80 mm in height. During the inelastic neutron scattering experiment the container was held in an aluminum vacuum furnace. Experiments were carried out in the temperature range of 340 to 460 °C for RbNO₃ or 270 to 400 °C for LiNO₃.

The neutron scattering experiment was performed on the medium resolution time-of-flight (TOF) spectrometer LAM-40², which is installed at the KENS pulsed neutron scattering facility (National Laboratory for High Energy Physics, Japan). On the inverted geometry spectrometer, pyrolytic graphite (PG, 002 reflection) is normally used as neutron analyzing mirrors. Under this operation mode, the energy resolution is about 200 μeV at elastic scattering position and the momentum transfer can be measured the range from 0.2 to 2.6 Å⁻¹. The LAM-40 has another set of analyzing mirrors using Ge 311 reflection. When the Ge mirrors are used, the energy resolution is about 900 μeV at elastic scattering position and the momentum transfer can be measured the wide range from 0.4 to 5.1 Å⁻¹. The Ge mirrors are suitable for investigating fast diffusive motions in a restricted space such as intra-molecular motions, because such motions show a broad quasielastic spectrum persisting into the high momentum transfer region. Multiple scattering correction³) was made to the observed scattering data by PG mirrors to obtain the dynamical structure factors S(Q,ω) at the temperatures mentioned above.

RESULTS AND DISCUSSION

Figure 1 shows the dynamical structure factors S(Q,ω) for RbNO₃ and LiNO₃ measured by PG mirrors. These S(Q,ω) were measured at 21 scattering angles between 13 and 120°. These figures show that modest undulations can be observed in the Q dependence around sharp quasielastic spectra. This suggests that the momentum dependence of the fast intra-ionic motion is existing in both systems.

We separated intra-ionic correlation and inter-ionic correlation on a quasielastic neutron scattering spectrum in the S(Q,ω). Diffusive motions in metal nitrate melts are classified
according to relaxation time scales. We consider that the intra-nitrate ionic motion is a rotational motion and the translational motion of a nitrate ion is diffusion of center of gravity of each ion. The latter has inter-ionic correlation. Usually the intra-ionic motion (characteristic relaxation time = $10^{-13}$ sec) is more rapid than the inter-ionic motion (characteristic relaxation time = $10^{-12}$ sec). Therefore the intra-ionic motion is thermally
averaged out in the time scale of inter-ionic motion. It is generally assumed that there is no correlation between translation and rotation of each ion. Furthermore it is supposed that nitrate ions rotate independently from one another. Based on the assumptions described above the dynamical structure factor $S(Q,\omega)$ is written as follows $^4$:

$$S(Q,\omega) = S^u_{\text{ion-ion}}(Q,\omega) + S_{\text{NO}_3-\text{ion}}(Q,\omega)$$

where $S^u_{\text{ion-ion}}(Q,\omega)$ is the coherent dynamical structure factor contributed from the inter-ionic correlations of three different kinds of pairs, i.e. cation-cation, cation-anion and anion-anion, and $S_{\text{NO}_3-\text{intra}}(Q,\omega)$ is the dynamical structure factor for intra-nitrate ionic motions.

Following the above consideration, Eq. (1) is empirically fitted to a model of Lorentz functions;

$$S(Q,\omega) = \frac{C}{\pi} \left\{ (1 - A) \frac{D_1 Q^2}{\omega^2 + (D_1 Q^2)^2} + A \frac{D_2 Q^2}{\omega^2 + (D_2 Q^2)^2} \right\}$$

Fig. 2. Quasielastic neutron scattering spectra of molten RbNO$_3$ at 340 $^\circ$C. (a) Spectrum measured by PG mirrors at $Q$=1.74 Å$^{-1}$; solid line represents the fitting result consisting of narrow (dotted line) and broad (broken line) quasielastic components. (b) Spectrum measured by Ge mirrors at $Q$=2.53 Å$^{-1}$; solid line represents the result fitted to broad quasielastic component.
where $A$, $D_1$, and $D_2$ are the parameters decided by a least-squared fitting. The first term ($D_1$ term) in Eq. (2) corresponds to narrow component in the spectrum describing the inter-ionic correlation. The broad component for intra-nitrate ionic correlation is represented by the second term ($D_2$ term) in Eq. (2).

Figure 2(a) shows that the model function Eq. (2) gives an excellent agreement with the experimental spectrum obtained by PG mirrors. Two Lorentzian components are shown in Fig. 2(a). The broad one corresponds to the intra-nitrate ionic motion and the narrow one the inter-ionic motion. An example of fitting the model function to the spectrum obtained by Ge mirrors is shown in Fig. 2(b), where we have fitted one Lorentz function to the broad component of spectrum. This Lorentz function refers to the intra-nitrate ionic motion.

The momentum dependence of energy-integrated intensity for broad component in spectrum is shown in Figure 3. The intensity has characteristic momentum dependence in oscillation. This feature comes from time correlations of atomic sites varied by the intra-nitrate ionic motion.

In order to explain the intra-nitrate ionic motion, we use rotational jump diffusion models, assuming that nitrate ion is a rigid one and its shape is a regular triangle. The center of gravity of a nitrate ion is on the nitrogen atom. Therefore we consider only the scattering from oxygen atoms when calculating the rotational motion of nitrate ion. Let us consider rotational jump between two equivalent sites, $m$ and $n$, of oxygen atoms around the nitrogen atom. The neutron intermediate scattering function $I(Q,t)$ can be evaluated,

$$
I(Q,t) = \langle \exp\left( i\mathbf{Q} \cdot \mathbf{r}(t) \right) \exp\left( -i\mathbf{Q} \cdot \mathbf{r}(0) \right) \rangle
$$

$$
= \sum_{m=1}^{2} \sum_{n=1}^{2} P(m,t;n,0) \cdot P(n,0) \sum_{j=1}^{3} \sum_{k=1}^{3} \exp\left( i\mathbf{Q} \cdot (\mathbf{r}_{jm} - \mathbf{r}_{kn}) \right), \quad (3)
$$

where $P(m,t;n,0)$ is the probability that the nitrate ion is found at site $m$ at time $t$ under the condition that it stayed at site $n$ at $t=0$. $P(n,0)$ denotes the probability that a nitrate ion is found at site $n$ at $t=0$. Now considering the equivalent two site model, $P(m,n)$ is equal to 1/2. Mark $j$ or $k$ shows each oxygen atom in the nitrate ion. The $r_{jm}$ and $r_{kn}$ denote the oxygen positions on the site $m$ or $n$ respectively. The probability $P(m,t;n,0)$ can be get easily by solving rate equations. Finally we obtain following equation:

$$
I(Q,t) = A_0(Q) + A_i(Q) \cdot \exp\left( -\frac{2t}{\tau} \right), \quad (4)
$$

Calculating the time Fourier transformation of time dependent term in $I(Q,t)$, the scattering law for rotational motion of a nitrate ion can be written,

$$
S_{NO_3-\text{intra}}(Q,\omega) = A_i(Q) \cdot \frac{1}{\pi} \cdot \frac{2\pi}{4 + \omega^2 \tau^2}, \quad (5)
$$
where $A_1(Q)$ is the term that shows the correlation between site n and site m. $A_1(Q)$ can be calculated by assuming the nitrate jump sites centered around nitrogen atom.

Calculating $A_1(Q)$ models are drawn by a solid line and a dashed line for comparison with the integrated intensity of intra-nitrate component in Fig. 3. The model (a) (the solid line) was calculated from the rotational two sites jump motion at a suitable angle with both sites centered around C\(_3\) axis on the nitrate ion. The model (b) (the dashed line) means the librational two sites jump motion centered around C\(_{2}'\) axis. The $Q$ dependence of energy-integrated intensity seems to be close to model (a). We have attempted to calculate another models having different angles between sites or various equiangular sites. However, the model (a) gives a most reasonable result, which implies that a nitrate ion in RbNO\(_3\) melt is subjected to the rotational vibration centered around C\(_3\) axis on the ion. MD simulation indicates that Rb\(^+\) ion is located on the plane of nitrate ion\(^6\). Such a location of Rb\(^+\) ions hinders the librational motion around C\(_{2}'\) axis and allows the rotational motion around C\(_3\) axis.

![Diagram](image)

Fig. 3. Momentum dependence of energy-integrated intensity for broad component of molten RbNO\(_3\) at 340°C. Solid line (a) represents $A_1(Q)$ calculated from the rotational two sites jump motion centered around C\(_3\) axis with $\theta=20^\circ$. Broken line (b) represents $A_1(Q)$ calculated from the librational two sites jump motion centered around C\(_{2}'\) axis with $\theta=45^\circ$. 

---

625
Fig. 4. Momentum dependence of energy-integrated intensity for broad component of molten RbNO₃ at 340 °C and LiNO₃ at 270 °C. Solid line represents the calculated $A_1(Q)$ from the rotational two sites jump motion centered $C_3$ axis with $\theta=20^\circ$. Broken line represents the calculated $A_1(Q)$ from the same motion with $\theta=14^\circ$.

A contrast between the intra-ionic motion in LiNO₃ melt and in RbNO₃ melt is shown in Figure 4. In either case the oscillating feature dose not change, namely, the nitrate ion moves within the framework of moving around $C_3$ axis on the ion. However the nitrate motion in LiNO₃ is the librational motion which amplitude is smaller than in RbNO₃ melt. This fact shows that the motion of nitrate ions in LiNO₃ is restricted strongly by surrounding cations.

REFERENCES

DOUBLE CRYSTAL DIFFRACTOMETER ARRANGEMENT FOR VERY SMALL ANGLE NEUTRON SCATTERING WITH PNO IN JRR-3M

Kazuya AIZAWA and Hiroshi TOMIMITSU

Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 JAPAN

ABSTRACT

The status of a double crystal diffractometer (DCD) for very small angle neutron scattering (VSANS), which is arranged in the precise neutron optics (PNO) apparatus on 3G beam hole at JRR-3M, is presented. The DCD consists of nondispersive (1,-1) setting of perfect silicon single crystals with a sample between two crystals and is set in a constant temperature chamber. The first crystal is set on a normal goniometer and acts as a horizontal beam collimator. The second crystal is set on a precise goniometer of which the smallest control step size is $5 \times 10^{-3}$ sec of arc, and acts as an analyzer for VSANS. The 111 symmetric reflection is used for both crystals. A measurement of silica spheres reveals that the q-range is available between $2 \times 10^{-4}$ and $3 \times 10^{-2}$ nm$^{-1}$, which covers up to $\mu$m in real space.

INTRODUCTION

Small angle scattering techniques using neutrons and X-rays have been widely used to investigate the structure in the range between 1nm and several $\mu$m. There are many slit type small angle neutron scattering (SANS) instruments combined with a cold neutron source and a two-dimensional position sensitive detector. These instruments achieve a small q ($q = 4\pi \sin \theta \lambda$, where $2\theta$ is the scattering angle and $\lambda$ is the neutron wavelength) by a long wavelength and a long sample to detector distance. On the other hand, there are another kind of instruments called DCD based on the dynamical theory of perfect single crystals. This method achieves a small q by high angular resolution. There are many applications of DCD for VSANS [1-6] since the pioneered work by U. Bonse and M. Hart [7] in the X-rays field. Because of high angular resolution, the main feature of DCD is that high resolution of q can be achieved without long sample to detector distance geometry, i.e., rather compact geometry. Here, high resolution of q means that an accessible minimum q is smaller than slit type SANS instruments. In this paper, we describe the DCD for VSANS at JRR-3M.

BASIC PROPERTY OF DCD

Figure 1 shows the schematic layout of the DCD. The DCD consists of nondispersive (1,-1) setting of perfect silicon single crystals with a sample between two crystals and is mounted on a vibration isolator that is set in a constant temperature chamber with $3.1m \times 3.5m$ dimensions, which typically keeps the temperature within room temperature $\pm 0.02^\circ$C.
Monochromatic incident neutrons reflected by (+,-) setting of pyrolytic graphite crystals enter a constant temperature chamber. Because of the double monochromator method, the incident beam goes through a same position independently neutron wavelengths. The first crystal is set on a normal goniometer. That crystal acts as a fine monochromator and a horizontal beam collimator. The second crystal is set on a precise goniometer of which smallest control step size is $5 \times 10^{-3}$ sec of arc, and acts as an analyzer for VSANS. The 111 symmetric reflection is used for both crystals. Analyzed neutrons are detected by a $^3$He counter through vacuum path.

![Diagram of neutron scattering setup](image)

Fig. 1. Schematic layout of the DCD for VSANS.

To obtain the basic property of the DCD, we measured the rocking curve without a sample at a neutron wavelength 0.15 nm, with a beam cross section of 10 mm$^W \times 30$ mm$^H$. The scan range of the rocking curve is divided into several parts of the different step size that becomes greater as an absolute value of the deviation from the Bragg angle increasing, e.g., the step size was 0.12 sec of arc around a peak and was 0.24 sec of arc in the outer parts of a peak and so on, and in the most outer parts, the step size was 3.84 sec of arc. This procedure enables a precise determination of intensity at a peak position and a wide range scan of $\Delta \theta$.

In the Bragg case, the reflection curve of a thick perfect crystal, $R(y)$, is expressed by the Darwin formula [3,6,8],

$$
R(y) = 1, \quad |y| \leq 1, \\
= 1 - \sqrt{1 - y^2}, \quad |y| > 1,
$$

where $y$ is the reduced angular parameter of the dynamical diffraction theory. In our setting, $y$ is given by

$$
y = k^2 v_c \sin 2\theta_b (\theta_b - \theta) / 16\sqrt{2} \pi b_c - \sqrt{2},
$$

where $k$ is the wave number, $v_c$ is the volume of the unit cell, $b_c$ is the coherent scattering length and $\theta_b$ is the Bragg angle. The rocking curve for our setting is expressed by the convolution of reflection curves, $i(\Delta \theta(y))[3,6]$ and the background, $B$,

$$
I(\Delta \theta) = Ai(\Delta \theta(y)) + B, \\
i(y) = \int R(y') * R(y - y') dy',
$$

---

628
where A is the scale factor, $\Delta \theta$ is the deviation from the Bragg angle ($\Delta \theta = \theta_0 - \theta$).

Figure 2 shows the measured rocking curve with the fitted curve by equation (3). The fitting was carried out on A, B and x-coordinate origin. Because we only need the deviation from a peak position in VSANS experiments, for graphical simple representation, the fitted x-coordinate origin, which is not the same as the Bragg angle generally, is transferred to a peak position.

Fig. 2. The measured rocking curve with the fitted curve by equation (3). (a) The profile around a peak. (b) The profile in a whole range.
The measured data is good agreement with the fitted curve in a whole range. Then, the following character is obtained. The full width at half maximum (FWHM) of the rocking curve is about 1.56 sec of arc, the maximum intensity at a detector position is about 1000 cps and the background is about 0.11 cps that is consistent with an actual background measurement. The signal to noise ratio (S/N) that means a ratio of the maximum intensity to the tail of the rocking curve is about $1 \times 10^4$.

**STANDARD SAMPLE MEASUREMENT AND ANALYSIS**

Powder of monodispersed silica spheres of diameter 1.05 μm (UBE-NIITO KASEI Co.) was measured, as a standard sample, to confirm the DCD performance. The measurement was done with the same condition mentioned previous section. The sample was put into a quartz cell of 1 mm thickness with 37% volume fraction. Figure 3 shows the scattering profile for the sample with a blank measurement (without sample run).

Fig. 3. The scattering profile for monodispersed silica spheres of diameter 1.05μm with the blank profile.

We can transform the measured data to the absolute macroscopic scattering cross section. It is well known that the (smeared) absolute macroscopic cross section, $d\Sigma(q) / d\Omega$ is

$$
\frac{d\Sigma(q)}{d\Omega} = \left( \frac{I_{\text{sample}}(q)}{Tr - I_{\text{cell}}(q)} \right) / I_{\text{blank}}(0) \Delta\theta_v \Delta\theta_h,
$$

(4)

where $I_{\text{sample}}(q)$, $I_{\text{cell}}(q)$ and $I_{\text{blank}}(q)$ are the sample, cell and blank background subtraction intensity, respectively, $Tr$ is the sample transmission, $\Delta\theta_v$ is the horizontal angular width which is the FWHM of $I_{\text{blank}}(q)$, $\Delta\theta_h$ is the vertical angular width which was calculated form geometrical setting and $t$ is the sample thickness. To evaluate $I_{\text{sample}}(q)$ from the sample data, it is necessary to carry out smoothing for the measured data and then the background subtraction
is carried out. Smoothing was carried out by a least-squares method of an algebraic polynomial [9]. This method determines the optimum number of neighbors for a given degree of polynomial. Also, we can substitute the value multiplied the fitted value of $I_{blank}(q)$ by cell transmission for the $I_{cell}(q)$, because small angle scattering does not occur from a cell, consequently the profile of the cell is similar except intensity, which we can correct by the cell transmission.

In our system, we must perform the slit height correction [10] to desmear the effect caused by the vertical divergence of the incident beam. Because of high angular resolution in the slit width direction, the slit width correction is not necessary. Then, the relation of the smeared macroscopic cross section, $d\Sigma(q)/d\Omega$, and the desmeared macroscopic cross section, $d\Sigma(q)/d\Omega$, is

\[
\frac{d\Sigma(q)}{d\Omega} = 2\int_0^\infty W(z) \frac{d\Sigma(\sqrt{q^2 + z^2})}{d\Omega} dz,
\]

\[
\int_{-\infty}^\infty W(z)dz = 1,
\]

where $W(z)$ is the weighting function in the slit height direction. For simplicity, the slit height correction was carried out by an iteration method [11]. We used the trapezoid weighting function calculated from geometrical setting. Figure 4 shows the measured and desmeared macroscopic cross section. The measurement covered the $q$-range between $2 \times 10^{-4}$ and $3 \times 10^{-2}$ nm$^{-1}$. The maxima for monodispersed spheres scattering function were clearly observed up to the third maximum. The behavior of $d\Sigma(q)/d\Omega \propto q^{-3}$ for the measured data and the behavior of $d\Sigma(q)/d\Omega \propto q^{-4}$ for the desmeared data, which are expected in the Porod region for the scattering bodies that have well-defined interface, are clearly shown.

![Graph](image)

**Fig. 4.** The VSANS intensity for silica spheres of diameter 1.05μm. The lower curve is the measured data. The upper curve is the desmeared data.
Next, the desmeared macroscopic scattering cross section was compared with the theoretical one. Our sample is slightly thick and rather high volume fraction of silica. Thus we must consider the multiple scattering effect and the interparticle interference effect. It is well known that the general form of the macroscopic cross section for monodispersed spheres of radius \( r \) is

\[
\frac{d\Sigma(q)}{d\Omega} = p \cdot \frac{4\pi}{3} r^3 [\Delta\rho]^2 F(q) S(q),
\]

where \( p \) is the volume fraction of spheres, \( \Delta\rho \) is the scattering length density difference between sphere and its environment, \( F(q) \) is the scattering function of sphere of radius \( r \) and \( S(q) \) is the interparticle interference function. And the form of \( F(q) \) is

\[
F(q) = \Phi^2(qr),
\]

\[
\Phi(qr) = \frac{3}{4} \left[ \frac{\sin(qr) - qr \cos(qr)}{(qr)^3} \right].
\]

Though it is difficult to select an adequate interparticle interference function, we considered a closed packed array model [12].

\[
S(q) = 1 + P \left( \frac{5 \sin(2qr)}{2qr} - 6\Phi(2qr) \right),
\]

where \( P \) is the packing parameter that varies between 0 for an infinitely dilute system and 1 for a closed packed array. Since negative value of \( S(q) \) appears in the case of \( P > 0.6 \), the value of \( P \) is restricted less than 0.6.

The multiple scattering effect is evaluated as follows [13]. First, the Fourier transform of the scattering probability which was multiplied the macroscopic cross section by the thickness, \( s(r) \), is evaluated.

\[
s(r) = 2\pi \int J_0(qr) r \frac{d\Sigma(q)}{d\Omega} q dq,
\]

where \( J_0(qr) \) is the zeroth order Bessel function of the first kind. Secondly, \( s(r) \) is transformed to \( h(r) \) by equation (10). \( h(r) \) is defined as the Fourier transform of the scattering probability affected the multiple scattering effect.

\[
h(r) = e^{-i0/k_0^2 k_0^2 (e^{-i(r/k_0^2)} - 1)}.
\]

Finally, The macroscopic cross section affected the multiple scattering effect, \( d\Sigma^*(q)/d\Omega \), is calculated by the inverse Fourier transform of \( h(r) \).

\[
\frac{d\Sigma^*(q)}{d\Omega} = \frac{1}{2\pi} \int J_0(qr) h(r) rdr.
\]

Unfortunately, the calculated curve for diameter 1.05\( \mu \)m, which is the nominal value evaluated from the scanning electron microscopy (SEM), was not agreement with the desmeared data. We tested several radii and \( P \). Figure 5 shows a comparison between the
The desmeared data and the model calculation in the case of diameter 0.95μm and $P = 0.5$. The calculated curve fairly agreed with the measured data except the range below $7 \times 10^{-3}\text{nm}^{-1}$, in which the interparticle interference effect dominates. The difference between the measured diameter and the calculated diameter is 9.5%. Though, we can't conclude whether the VSANS measurement contains an error or the SEM observation contains an error, we think that the VSANS measurement was carried out within 10% accuracy. The result shows that the absolute correction and the desmearing process were correctly performed.

![Graph showing desmeared data and calculated curve](image)

**Fig. 5.** A comparison between the desmeared data of silica spheres and the model calculation.

**CONCLUSION**

When we use the DCD at the neutron wavelength 0.15nm, the basic property is as follows: (1) The FWHM of the rocking curve is about 1.56 sec of arc. (2) The maximum intensity at a detector position is about 1000 cps. (3) The background is about 0.11cps. (4) The S/N ratio is about $1 \times 10^4$. Our DCD covers the q-range between $2 \times 10^{-4}$ and $3 \times 10^{-2}$ nm$^{-1}$. This very small q-range is often interesting in material science, etc., and the complementary use of the DCD and slit type SANS instruments will cover the wide q-range.

**REFERENCES**

PHASE SEPARATION AND ORDERING PROCESS IN Al-Li ALLOYS STUDIED BY SMALL-ANGLE NEUTRON SCATTERING AND NEUTRON DIFFRACTION

*M. Furusaka, +S.-I. Fujikawa and #J. M. Tranquada

*BSF,
National Laboratory for High Energy Physics (KEK)
Tsukuba-shi, 305 Japan

+Department of materials science
Tohoku University
Sendai, 980 Japan

#Physics Department
Brookhaven National Laboratory
Upton, New York 11973

ABSTRACT

To study phase separation kinetics of Al-9.5at%Li polycrystalline alloys in which precipitates have ordered Al₃Li (8') structure, profile analysis of small-angle neutron scattering and superlattice reflections {100} and {110} were done. A small-angle scattering instrument and a triple-axis spectrometer in elastic mode were used in the measurements. Strong texture was observed in the reflections. Therefore, measurements were done using the crystal orientation where the intensity of the reflection was at the maximum. Profiles of small-angle scattering and superlattice reflections were almost identical at higher momentum transfer side. At lower momentum transfer side, small-angle scattering showed interference effects, but superlattice reflection did not show any sign of the interference. Integrated intensities of superlattice reflections were obtained, and compared with the small-angle scattering intensity. The order parameter was not saturated in the 8' precipitates at the early stage of the phase separation process.

INTRODUCTION

Al-Li based alloys have gathered strong interest especially in the aircraft industry because of high strength, high elastic modulus and low density. They are also suitable to study kinetics of the phase separation behavior associated with ordering, since the misfit strain between the precipitates and matrix is very small. Precipitates at late stages are known to be metastable spherical Al₃Li (8'), but the mechanism of the formation of 8' precipitates and their ordering at earlier stages is not well understood.
Yu and Chen have studied early stages of decomposition processes as well as ordering kinetics for Al-Li systems by means of X-ray small-angle scattering and the superlattice reflection \{100\} measurement.\(^1\) They measured time dependence of integrated intensities and FWHM of superlattice reflection. They concluded that the onset of the ordering process is sooner than that of the decomposition processes for the Al-12at\%Li alloy in the temperature range from 180 C to 290 C.

Similar measurements have been done by Blaschko, Glas and Weinzierl using a small-angle neutron scattering (SANS) instrument and a triple axis spectrometer.\(^2\) They also provided intensity and size information for both quantities, but little discussion were given on the correlation between them. Interference effects in the \{100\} superlattice reflection were also found at short annealing times at 120 C, but because of the high background, counting statistics of the superlattice reflection was not enough to discuss the profiles of the peaks. To understand the mechanism of phase separation processes associate with ordering, we have to compare both quantities more quantitatively. Therefore, we performed profile analysis of both by using a triple axis spectrometer and a small-angle scattering instrument. We stated the phenomena from the time range when density fluctuations were very small, but ordering already takes place during quenching.

**EXPERIMENTAL PROCEDURES**

Al-9.5at\%Li alloys were cut into plates of 10\(^{w}\) x 30\(^{h}\) x 2\(^{t}\) mm\(^3\) and three of them were used for the neutron experiment. Solution treatment was performed at 500C followed by rapid quench into iced brine. Samples were then annealed for 1, 2, 4 hours at 100 C, and 20 minutes up to 24 hours at 150 C.

Superlattice reflections were measured at ambient temperature using H9 triple-axis spectrometer in elastic mode at Brookhaven National Laboratory BNL. Incoming neutron energy was 5 meV and collimation was 60'-40'-60'-80'-80'. Instrumental resolution \(8Q\) around the \{100\} was 0.012 A\(^{-1}\), which was about one order of magnitude better than the superlattice reflections. The scattering data were corrected for background and sample transmission.

Small-angle neutron scattering was carried out also at ambient temperature using the small-angle scattering instrument SAN at pulsed cold neutron source at National Laboratory for High Energy Physics (KEK). Sample to detector distance was 1m, which covered 0.02 \(\leq Q \leq 0.6\) A\(^{-1}\). The scattering data were corrected for background, sample transmission and normalized by incoherent scattering from pure water.

**RESULTS AND DISCUSSIONS**

Figure 1 shows typical results of texture measurement of \{100\} superlattice reflection in the Al-Li samples. Scattering angle was fixed at the center of each Bragg peak, and the sample was rotated along the vertical axis. The origin of the axis was fixed in such a way that the incident neutron beam direction was normal to the plates of the sample when scattering angle 2\(\theta\) was zero.
Fig. 1. Texture measurement of \{100\} superlattice reflection.

The analysis showed that there were two sets of crystallites. One of them aligned to one of the \{001\} axes were along the long direction of the specimen, one in the plane and one perpendicular to the face of the plates. The other set was such that \{111\} is along the long direction of the specimen and other \{111\} axes did not have specific angular preference. We decided to measure the superlattice reflection at the peak of such curve at fixed crystal orientation, as opposite to rotate the sample during the measurement as Blaschko et al. did in their experiment. The intensity gain by this method was more than twice, and we could eliminate the possibility of superposed background from different set of crystallites.

The \{100\} peak was measured in reflection geometry. Sample was rotated by 45 degrees to measure the \{110\} superlattice peak.

Figure 2 shows time evolution of \{100\} superlattice peak for 100 C and 150 C annealing temperature. Figure 3 shows SANS in linear scale for samples annealed at 150 C. The superlattice reflection was already evolved in the as quenched sample, but SANS was quite low in the $0.04 \leq Q \leq 0.4$ A$^{-1}$ range. Excess SANS was observed below $Q = 0.04$ A$^{-1}$, and it showed $I(Q) \sim Q^{-2}$ behavior, therefore, it could attribute to a scattering from grain boundaries.

Fig. 2. Time evolution of \{100\} superlattice peaks for 100 C and 150 C annealing.

Fig. 3. SANS profiles in 150 C annealed sample.
To compare the profiles of these superlattice reflections from (100) and (110), and SANS more precisely, they were plotted on the same figures as shown in Figs. 4, 5 and 6 in logarithmic scale. The abscissa of the scattering curves of the superlattice reflections was measured from the center of the peaks of the superlattice reflection, and constant background was subtracted from them. SANS curves were scaled so that the high-Q parts of them were overlapped with superlattice peaks.

As shown in Figs. 4, 5 and 6, superlattice reflections were smoothly falling down as Q increase and no sign of interference effect was observed as opposite to the result of Blaschko, Glas and Weinzierl. In contrast to it, SANS showed broad maxima; they could be attributed to the inter-particle interference effects between the precipitates. It is note worthy that higher Q part of both curves was almost identical. The SANS curves could be separated into form factor part and inter-particle interference part. Since there was no other source of scattering other than the precipitates, it is natural to think that form factor part of the SANS scattering is identical to that of superlattice reflections.

Then why the superlattice peaks did not show interference effects? The Al-Li alloy has fcc structure and there are four kinds of antiphase domains. Since nearest neighbor precipitates around one particular precipitate should take one or four antiphase domains at random, the interference term could be suppressed. On the other hand, since SANS reflects only smeared concentration fluctuation, all the nearest neighbor precipitates contribute to the interference term.

The high Q part of both curves showed nearly I(Q) ~ Q^-4 behavior, which corresponds to the formation of sharp interfaces between precipitates and the remaining matrix phase. It is well known that dynamical-scaling holds in such time range, at least in good approximation. In Fig. 7 shows the result of the dynamical scaling. A first moment of the scattering function Q, (almost same as a peak position of the scattering) was taken as the inverse of the relevant length scale. In the time range when dynamical-scaling holds, integrated intensity of SANS remains constant.
Fig. 6. Comparison of profiles of superlattice reflections (100) and (110), and scaled SANS in the 2 h annealed sample at 150°C.

Fig. 8 shows time evolution of integrated intensity of the (100) peak annealed at 150°C. It is an increasing function of annealing time. The integrated intensity is a measure of Li atoms at one of four sublattices over all the crystal. Since degree of order in the matrix phase is at least decreasing function of time, the order parameter inside the precipitates should increase with time.

Since integrated intensity of SANS remains constant, but that of superlattice reflection is increasing, the precipitates have lower order parameter than the stoichiometric δ' structure at the early stages. In as quenched sample, SANS is very low, reflecting very low density fluctuation, but order parameter over the entire system was already at significant level. These results may suggest that congruent or spinodal ordering may take place in the as quenched stage. Since the superlattice reflections show considerable broadening, there is no long-range order in the system; there should be many small ordered domains belongs to one of the four antiphase domains.

CONCLUSIONS

In conclusion, we observed superlattice peak even at the as quenched stage when SANS is still very low. The shape of ordered domain and that of precipitates were almost identical. At early stages, precipitates were not

Fig. 7. Dynamical scaling result of the 150°C annealed sample.

Fig. 8. Time evolution of integrated intensity of the (100) peak annealed at 150°C.
stoichiometric $\delta'$, but the degree of order was lower than the stoichiometric concentration.

We are grateful to Sumitomo Light Metals Ind. Ltd. for the preparation of specimens. The present work was partly supported by the Light Metals Educational Foundation of Japan, and by the U.S.-Japan Cooperative Neutron Scattering Program.

REFERENCES

IS THERE ANY CORRELATION BETWEEN THE INTERMOLECULAR STRUCTURES AROUND MAIN-GROUP METAL ION IN LIQUID AND CRYSTALLINE STATES?

K. ICHIKAWA, *Y. KAMEDA and *S. KOTANI
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

ABSTRACT

We have determined the environmental structure around a metal ion and the orientational conformation among the complex ions in liquid state, such as the environmental structure around Li⁺ in ionic or incompletely hydrated-ionic melts and the intermolecular geometry among NO₃ ion and AlCl₃ ions with the aid of time-of-flight neutron diffraction and isotopic substitution techniques. The space and time average local structures in liquid state do not reflect any crystal structure. Because the lattice energy of ionic crystal should be interpreted in terms of the Madelung constant: the energy of ionic melts or incompletely hydrated-ionic melts can be determined by the local configuration around an ion.

INTRODUCTION

Many diffraction experiments on ionic melts [1,2] and concentrated aqueous solutions[3] and molecular liquids[4] have simply determined one-dimensional structure features of the melts such as intra- or intermolecular distances and coordination numbers. It is of much interest to elucidate the environmental structure around a metal ion and the orientational conformation among the complex ions in liquid state.

We have proposed the environmental structure around Li⁺ and the intermolecular geometry among metal complexes in molten LiAlCl₃[5], molten LiNO₃[6], and incompletely hydrated LiCl melt[7] or CD₂COOLi melt[8], with the aid of the neutron diffraction and isotopic substitution techniques. Enderby et al. developed these techniques to investigate for the first time the nature of hydration around Li⁺ in concentrated aqueous solutions[9].

In this paper we will compare the local structure of short-range order observed in liquid matter with the structure of ionic crystal as well as hydrated-ionic crystal. The discussion will be opened on the correlation between the structures for both crystal and melt.

Present address:*Yamagata University and *Steel Nippon Co.
THEORY

When the ionic melt of LiNO₃ is taken as a typical instance, the observed total scattering cross section taken from a neutron diffraction experiment is divided into two parts corresponding to coherent and incoherent contributions[6]. The observed coherent term is divided into self and interference terms

\[
\frac{d\sigma}{d\Omega}_{\text{coh}} = \frac{d\sigma}{d\Omega}_{\text{coh}}^\text{self} + \frac{d\sigma}{d\Omega}_{\text{coh}}^\text{int}. \tag{1}
\]

The self term, scaled by a molecule formulated as LiNO₃, is written as

\[
\frac{d\sigma}{d\Omega}_{\text{coh}}^\text{self} = b_1^2 + b_2^2 + 3b_0^2, \tag{2}
\]

where \(b_i\) denotes the coherent scattering length of nucleus \(i\). The interference term consists of the contributions from the intramolecular and intermolecular parts. The intramolecular interference term, which is the scattering from an isolated complex ion NO₃⁻, can be expressed as

\[
\frac{d\sigma}{d\Omega}_{\text{coh}}^\text{int} = 6b_N b_0 \exp (-\frac{l_{10}^2 Q^2}{2}) \frac{\sin(Qr_{10})}{Qr_{10}} + 6b_0^2 \exp (-\frac{l_{20}^2 Q^2}{2}) \frac{\sin(Qr_{20})}{Qr_{20}}. \tag{3}
\]

Where \(l_y\) and \(r_y\) denote the root mean square amplitude and the internuclear distance of nuclear pair \(y\), respectively. The intermolecular interference term consists of six weighted partial structure factors \(a_{y}(Q)\),

\[
\frac{d\sigma}{d\Omega}_{\text{coh}}^\text{int} = b_1^2 [a_{LL}(Q) - 1] + b_2^2 [a_{NN}(Q) - 1]
+ 2b_1 b_2 [a_{LN}(Q) - 1] + 6b_N b_0 [a_{NO}(Q) - 1]
+ 6b_1 b_0 [a_{LO}(Q) - 1] + 9b_0^2 [a_{OO}(Q) - 1]. \tag{4}
\]

Environmental structure around Li and N

We introduce the differences \(\Delta_{Li}(Q)\) and \(\Delta_{N}(Q)\) between the two intermolecular interference terms of (4); they are identical in all respects except that the isotopic composition of the Li or N nucleus has been changed[5–9]. The difference \(\Delta_{Li}(Q)\) or \(\Delta_{N}(Q)\) consists of the three terms, i.e.,

\[
i\Delta_{i}(Q) = (b_i^2 - b_i'^2) [a_i(Q) - 1] + 2b_i(b_i - b_i')[a_{i'}(Q) - 1]
+ 6b_0(b_i - b_i')[a_{i'}(Q) - 1]. \tag{5}
\]

where \(i=Li\) and \(j=N\) (14 or 15) for \(\Delta_{Li}(Q)\), or \(i=N\) and \(j=Li\) (6,7 or 7) for \(\Delta_{N}(Q)\); \(i\) and \(i'\) correspond to the different isotopic compositions for nucleus \(i\). The Fourier transforms of \(\Delta_{i}(Q)\) and \(\Delta_{i'}(Q)\) give the distribution functions \(G_{Li}(r)\) and \(G_{N}(r)\) around Li⁺ and N. They are expressed as the weighted sum of three partial pair distribution functions \(g_{ij}(r)\) as follows:

\[
i'G_{i}(r) = (b_i^2 - b_i'^2) [g_{i}(r) - 1] + 2b_i(b_i - b_i')[g_{i'}(r) - 1]
+ 6b_0(b_i - b_i')[g_{i'}(r) - 1]. \tag{6}
\]
RESULTS AND DISCUSSION

We have carried out the time-of-flight (TOF) neutron diffraction measurements for a couple of melts which are identical in all respects except that the isotopic state of Li or N by using a high intensity total scattering spectrometer (HIT) installed at the pulsed spallation neutron source of KENS[10].

It is very interesting to compare the environmental structure around Li⁺ and the orientational configuration among complex anions, which have been for the first time determined with the aid of isotopic substitution technique, in the ionic and incompletely hydrated-ionic melts, with the long-range order structure for their corresponding ionic or hydrated-ionic crystals such as (1) LiNO₃, (2) CH₃COOLi·2H₂O, (3) LiCl·H₂O and (4) LiAlCl₄ as follows:

(1) In the LiNO₃ melt Li⁺ is surrounded tetrahedrally by four nitrate ions and one oxygen atom in each of these four NO₃⁻ faces towards Li⁺ as shown in fig. 1a. In the crystalline state of LiNO₃ salt, Li⁺ is sandwiched between the layers formed by NO₃⁻ ions (see fig. 1b).

(2) In the incompletely hydrated melt of CD₃COOLi the two oxygen atoms in a CD₃COO⁻ are equivalent from Li⁺ and the first hydration is deficient in water molecules hydrated around Li⁺ (the hydration number is 3.0±0.3) as shown in fig. 2a: In the crystalline state of CH₃COOLi·2H₂O the two oxygen atoms, which locate at the first nearest neighbour distance of Li⁺, belong to the two different acetate anions (see fig. 2b).

(3) Both direct and indirect Li−Cl correlations have been observed in the incompletely hydrated LiCl melt as shown in fig. 3a: the four chloride anions are equivalent from Li⁺ in the crystal of LiCl·H₂O (see fig. 3b).

(4) In the LiAlCl₄ melt Li⁺ is surrounded by ca. eight chlorine atoms. Li⁺ locates at the center of the six AlCl₄⁻ ions. The possible configuration among the nearest neighbour AlCl₄⁻ anions is similar to that for liquid VCl₄[11] as well as CCl₄[4] as shown in fig. 4.

The local structure in liquid state demonstrates that the chemical short-range structure in environment around a metal ion as well as the intermediate-range structure among complex ions is characteristic of the structural unit of tetrahedron which has 4 atoms/molecules or 4 complex ions and a metal ion in the central site. The space and time averaged local structure in the liquid state does not reflect the crystal structures. Because the lattice energy of ionic crystal should be interpreted in terms of the Madelung constant: the energy of ionic melts or incompletely hydrated-ionic melts can be evaluated by the orientational conformation around an ion.

ACKNOWLEDGEMENT

We wish to thank Professors N. Watanabe and M. Misawa (KENS), and T. Fukunaga (Nagoya Univ.) , who are responsible for a HIT installed at the spallation neutron of KENS in Japan, for his encouragement during the course of this work.
REFERENCES

Fig. 1a. The possible local structure around Li⁺ and orientational configuration among NO₃⁻ ions for molten LiNO₃.

Fig. 1b. The crystalline structure of LiNO₃.

Fig. 2a. The possible local structure around Li⁺ for incompletely hydrated CD₃COOLi melt. There is a CD₃COO⁻ above Li⁺ and the three water molecules below it.

Fig. 2b. The crystalline structure of CH₃COOLi·2H₂O.
Fig. 3a. The possible local structure around Li\(^+\) for incompletely hydrated LiCl melt. There are a chloride anion and the three water molecules around Li\(^+\).

Fig. 3b. The crystalline structure of LiCl-H\(_2\)O

Fig. 4. The possible local structure around Li\(^+\) and orientational configuration among AlCl\(_4^-\) ions for molten LiAlCl\(_4\).
SMALL ANGLE NEUTRON SCATTERING STUDY OF SILICA SUSPENSIONS


#Department of Chemistry for Materials, Faculty of Engineering, Mie University
1515 Kamihama-cho, Tsu-shi, Mie-ken 514 Japan

*Department of Physics, Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

+Macromolecular Research Laboratory, Faculty of Engineering,
Yamagata University
Jyo-nan, Yonezawa-shi, Yamagata-ken, 992 Japan

ABSTRACT

Two types of silica were used: one is Aerosil-130 silica, which is easily aggregated in water and the other is Snowtex-C dispersed in water. These silicas were mixed with an aqueous solution of hydroxypropyl methyl cellulose (HPMC) that adsorbs on the silica surfaces to make silica suspensions. Small angle neutron scattering (SANS) technique was used to understand the structures and interactions of the silica suspensions and the corresponding silica slurries (no HPMC) as functions of HPMC and silica content. The wave vector q was ranged 0.03 to 0.8 nm⁻¹. In the scattering curves for Aerosil silica slurries and suspensions below q = 0.1 nm⁻¹, a power-law exponent of 2.1 was obtained independent of silica content. The scattering curves at higher q, however, approached a power-law scattering with an exponent of -4, namely followed the Porod's law. It was found that adsorption of HPMC did not effect on the scattering curves. On the other hand, for Snowtex-C the peak was observed at the intermediate q in the scattering curves, whose position shifts to higher q with an increase in silica content, indicating that an average distance between silica particles decreases. Snowtex-C suspensions showed an increase in scattering intensity below q = 0.1 nm⁻¹ by adsorption of HPMC.

INTRODUCTION

Understanding of the structures and interactions in colloidal dispersions has recently advanced due to the application of small angle neutron scattering (SANS).¹ In SANS measurements many different types of colloidal system have been used, such as the dispersions of latex particles,² oxide sols,³,⁵ and clay.⁶ Among the oxide sols silica particles were often adapted since their characteristics were relatively known. Aggregation behavior of the silica particles dispersed in
water strongly depend on pH. At pH = 2 the silica particles carry zero charge on the surface and below pH = 2 the silica particles become positively charged and meta-stable. On the other hand, above pH = 2 the silica particles own negative charge and they tend to aggregate with an increase in pH. In the range pH 8-10 repulsion forces lead to stable silica dispersions and the silica particles dissolve in water beyond pH = 11.

In this study, we investigated the structural changes in the silica particles dispersed in water and in aqueous solution of polymer chains that adsorb on the surfaces of the silica particles in terms of the distances between the silica particles obtained from the SANS measurements.

**EXPERIMENTAL**

**Materials** We used two silicas. Aerosil-130 supplied from Aerosil Japan (Yokkaichi) was fumed silica. From the manufacture, the surface area is 141 m²/g and the particle diameter is 16 nm. It was dried in a vacuum oven at 200°C. Snowtex-C dispersed in water, which is a typical colloidal silica due to repulsion forces between negative charges on silica surfaces was supplied from Nissan Chemical Co. and its diameter is ranged 10 to 20 nm. It was used without further purification.

HPMC sample of 65SH-400 supplied from Shin-Etu Chemical Co. was purified by precipitation of its aqueous solutions containing 0.02% NaN₃ into acetone and freeze-dried from its aqueous solution. The molecular weight of HPMC was determined from the intrinsic viscosity measurements in aqueous 0.1 N NaCl solution at 25 ± 0.05°C using an Ubbelohde viscometer. The molecular characteristics were as follows: the molecular weight (Mw) of HPMC is 403 x 10³, the degree of substitution (DS) of OCH₃ group is 1.8, and the molar substitution (MS) of OC₃H₇OH group is 0.15.

Water purified by a Millipore Q-TM system was used. Pure grade quality NaN₃ was used as a preservative for HPMC.

Silica slurry of Aerosil-130 was prepared by dispersing the silica powder in water by mechanically shaking and ultrasonic irradiation and the resulting silica slurry was turbid. An aqueous solution of HPMC with known concentration was added to the resulting silica slurry and the mixture, hereafter called as the silica suspension was mixed well by mechanically shaking and by further ultrasonic irradiation to obtain a homogeneous mixture.

On the other hand, Snowtex-C dispersion was mixed with an aqueous HPMC solution to prepare a desired mixture by mechanically shaking. Silica content was ranged 2.5 to 10 wt. % and HPMC concentration was fixed 1.5 wt. % for the respective silica content.

**SANS Instrument** SANS experiments were performed using the JAERI 20 m SANS instrument. The wavelength λ was selected to be 0.625 nm by using a velocity sector with variable speed and pitch and the wavelength resolution is Δλ/λ = 15%. The monochromatic beam was collimated by a series of circular apertures of diameter 10 mm. The 5 mm circular aperture was suited before the sample cell to define the sample illuminated. The samples were transferred to quartz cells of path length 1 mm. The scattered neutrons were detected by a ³He area detector of 58 cm diameter circle containing 128 pixel elements. The sample to detector distances were 3 and 10 m, corresponding to the wave vector q range 0.03 to 0.8 nm⁻¹. The measuring temperature was 25 ± 1°C. Data were corrected
for empty cell background. Data taken at 3 m sample to detector distance cover the
q range 0.09 to 0.8 nm\(^{-1}\) and data at 10 m range from 0.03 to 0.25 nm\(^{-1}\).

RESULTS AND DISCUSSION

Adsorption study of HPMC on silica surfaces was reported in a previous paper.\(^{10}\) The adsorption isotherm was a rounded-shape isotherm because of the polydispercity of HPMC sample. The adsorbed amount of HPMC at the plateau region was 0.1 g/g. As a concentration of HPMC studied here was well in the plateau region of the adsorption isotherm of HPMC, silica particles were saturated with HPMC chains and free HPMC chains were remained in water.

**Aerosil Silica-130** As mentioned above, the appearance of turbidity in the silica slurry shows aggregation of silica particles in water. Figure 1 shows the scattering intensity I(q) as a function of q for two silica slurries of 2.5 and 7.5% silica content. The intensity at low q range decreases with an exponent of -2.1, namely corresponding to the fractal dimension and at high q region I(q) tends toward the Porod’s law, irrespective of the silica content. Similar scattering curves were obtained the silica slurries of 5.0 and 10%. This indicates that the silica slurry is a kind of fractal object and its structure is self-similarity. However, the resulting fractal dimension does not agree with the two most popular models,\(^{11}\) diffusion-limited aggregation and diffusion-limited cluster-cluster aggregation. Similar fractal dimension was obtained for the colloidal aggregates of silica particles by addition of salt.\(^{12}\) The exponent of -4 at high q range can be interpreted by scattering from the individual silica particles making up the aggregates. Therefor, from the q value at which the crossover occurs between the two exponents, we can calculate nominal radius of gyration of silica particle, 5.8nm.

![Figure 1](image_url)

**Figure 1.** Double logarithmic plots of scattering intensity I(q) against q for the Aerosil-130 silica slurries: (□) 2.5% silica content; (○) 7.5% silica content.
In Figure 2, the scattering curves of the 2.5 and 7.7% silica suspensions are displayed. They are superimposed to those of the corresponding silica slurries without any correction. This means that the addition of HPMC to the silica slurries does not induce any changes in the aggregated structures of silica particles dispersed in water, although adsorption of HPMC on the silica particles occurs.

Figure 2. Double logarithmic plots of scattering intensity $I(q)$ against $q$ for the Aerosil-130 silica suspensions. Symbols are the same as in Figure 1.

Figure 3. A Guinier plot of Aerosil-130 silica suspension of 7.5% silica content.
To deduce the average size of the particles dispersed in medium, the Guinier approximation is sometimes used for uniform particles of any shape. A typical Guinier plot of the 7.5% silica slurries is represented in Figure 3. It clearly indicates that there is no distinctive linear behavior. This suggests that either the particles are too polydisperse in size or that the Guinier region is not covered in the experiment. In either case, no structural information can be extracted from the Guinier plot as far as our data are concerned. Since a detailed structural analysis taken into account polydispersity is needed, such an analysis is under proceeding and some results will be appeared in the future.

Figure 4. Scattering intensity $I(q)$ as a function of $q$ for various Snowtex-C dispersions: (□) 2.5% silica content; (△) 5.0% silica content; (○) 7.5% silica content; (△) 10% silica content.

Snowtex-C

Figure 4 shows the scattering curves of Snowtex-C dispersions of 2.5, 5.0, 7.5 and 10% silica content. In the respective scattering curves a peak was observed. The peak shifts to high $q$ systematically with the silica content: the more silica content, the shorter the distance of separation between neighboring spheres. The separation distances calculated from the Bragg's relation, $D = 2\pi/q$ are 48.3, 40.5, 36.9, and 33.8 nm for the colloidal silica dispersions of 2.5, 5.0, 7.5 and 10% silica content, respectively. These separation distances are compared with the average distance ($d$) calculated from the relation $d = (4\pi\rho/3C)^{1/3}$ based on a simple model, where $\rho$ is the density of silica (2.2 g/cm$^3$) and $C$ is the silica concentration in the dispersion. Such average distances are 57.4, 45.5, 39.8, and 36.1 nm for the corresponding silica dispersions. Their values are in good agreement with those obtained from the SANS measurements.

In Figure 5 the scattering curves of colloidal silica dispersions of 2.5, 5.0, 7.5, and 10% silica content in aqueous HPMC solution are displayed as a function of $q$. A comparison of the scattering curves in Figures 4 and 5 shows that broadening in
Figure 5  Scattering intensity I(q) as a function of q for various Snowtex-C dispersions in aqueous HPMC solution. Symbols are the same as in Figure 4.

the peak occurs and the scattering intensity at lower q range increases by adsorption of HPMC. This means that the short-range order resembling a crystal becomes loosing by screening the electrostatic repulsions forces between the silica particles, leading to formation of the large size aggregates in the dispersions.

REFERENCES

CHAIN CONFORMATIONS OF ABA TRIBLOCK COPOLYMERS IN MICROPHASE-SEPARATED STRUCTURES FOR SANS

*Y. MATSUSHITA, °M. NOMURA, °J. WATANABE, °Y. MOGI, 
°I. NODA and °C. C. HAN

°Department of Applied Chemistry, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-01 Japan

*Materials Science and Engineering Laboratory,
National Institute of Standards and Technology,
Gaithersburg, MD 20899, U.S.A.

ABSTRACT

Single chain conformations of center block, polystyrene, of poly(2-vinylpyridine-b-styrene-b-2-vinylpyridine)(PSP) triblock copolymers of the ABA type in bulk were measured by small angle neutron scattering (SANS), while microphase separation structures were studied by small angle X-ray Scattering (SAXS) and transmission electron microscopy (TEM). From the morphological observations, PSP block copolymers have confirmed to have alternating lamellar structure both when $\phi_s=0.33$ and $\phi_s=0.5$, where $\phi_s$ is the volume fraction of polystyrene blocks. It was also clarified that the chain dimension of center blocks of sample with $\phi_s=0.33$ is smaller than that of sample with $\phi_s=0.5$. This result may mean that the center blocks have bridge-rich conformation when $\phi_s=0.33$ while they have loop-rich conformation when $\phi_s=0.5$.

INTRODUCTION

Microphase separation structures of block copolymers have been extensively studied for AB diblock copolymers both experimentally and theoretically. Morphology change with composition of the component blocks was believed to obey the Molau's rule which involves spherical, cylindrical and alternating lamellar structure for a while$^{1-3}$. However, recently a new
morphology called tetrapod structure\textsuperscript{4}) or ordered bicontinuous double-diamond (OBDD) structure\textsuperscript{5,6} has found and reported.

Recently, chain conformations of block copolymers have measured in several works for AB diblock copolymers by SANS\textsuperscript{7-9).} Alternating lamellar structure was chosen in most of the conformation study because this structure is geometrically the simplest one and can be conceived to be a equilibrium structure over the others, of which the domain structures are easy to suffer from nonequilibrium effects encountered in the domain formation process. In this structure, block chain is known to be contracted toward the direction parallel to lamellar interface to compensate the elongation along perpendicular direction\textsuperscript{9).}

Many works are known on the study of the morphology of triblock copolymers. Among them, Uchida et al.\textsuperscript{10)} has found that styrene-isoprenestyrene triblock copolymers reveal alternating lamellar structure if the volume ratio of S:I:S is 1:2:1 and Helfand and Wasserman\textsuperscript{11)} predicted that the lamellar domain spacing of ABA triblock copolymers is almost the same as that of diblock copolymers of A-1/2B type theoretically. Recently Quan and Koberstein\textsuperscript{12)} measured the chain dimension of polybutadiene part of styrene-butadiene-styrene triblock copolymers by SANS and found that the overall all radius of gyration of the center block is a little larger than that of the unperturbed chain.

In this work we have focused on the chain conformations of the center blocks of ABA triblock copolymers and have studied the lamellar structure for the same reason as described above. The structural feature of this copolymer in bulk is that the center block have to choose loop-type conformation or bridge-type one, therefore this restriction may affect the microdomain structure formation.

**EXPERIMENTAL**

Samples used were polymerized by an anionic polymerization with dipotassium salt of \( \alpha \)-methylstyrene tetramer as a bifunctional initiator in THF. Several PSP polymers with different compositions from S/P=1/1 to S/P=1/2 were prepared first to observe the morphological features their molecular characteristics were shown in Table I. The number average molecular weights of samples were measured by membrane osmometry, the apparent molecular weight distributions were estimated by gel-permeation chromatography and compositions were determined by pyrolysis-gas chromatography as described previously.\textsuperscript{13)} Secondly, deuterium-labeled polymers, poly(2-vinylpyridine-styrene-d8-2-vinylpyridine) (PDP) were prepared adjusting the chain lengths and composition to those of unlabeled PSP
for conformational study. Their molecular characteristics were shown in Table II.

Films for morphological observations and for SANS study were cast from dilute solutions of THF, which is a common good solvent for both components, dried under vacuum and then annealed at 120°C for 10 days. PSP/PDP blend ratios were somewhat different among samples so as to have 11/89 mixtures by volume in terms of polystyrene, this S/D ratio corresponds to the matching ratio of scattering length density between polystyrene phase and poly(2-vinylpyridine) phase.

Microphase separation structures were observed by transmission electron microscopy for osmium tetroxide-stained sample films and by SAXS. Small-angle X-ray scattering was carried out from two directions, one is the edge-view where X-ray beam was irradiated parallel to the film surface the other is the through view where radiation is going through normal to the film surface.

SANS experiment were performed by using SANS facility at the National Institute of Standards and Technology with a two dimensional position-sensitive detector\(^{14}\). The wavelengths used was 9Å and sample-detector distance was 3.5m. The measurement were carried out from through view only, and the scattering intensity were averaged circularly since isotropic two-dimensional contour maps were observed for every blend films.

### RESULTS AND DISCUSSION

Typical microphase separation structures are shown in Figure 1. It is clear from these micrographs that both PSP-3 (\(\phi_s=0.50\)) and PSP-5 (\(\phi_s=0.33\)) reveal alternating lamellar structures. Samples PSP-2 (\(\phi_s=0.42\)) and PSP-4 (\(\phi_s=0.37\)) were also confirmed to have lamellar structures though they were not shown here. SAXS diffraction patterns from edge view measurements were compared in Figure 2 for four samples. Integral number order peaks owing to lamellar structures were shown for all patterns, however, the second order peak is missing for PSP-3, while the third order peaks missing for PSP-
5. These facts can be explained by considering the electron density profiles of samples and their particle scattering factors. In short, the even-number order peaks should disappear if the thickness of a $S$ lamella and a $P$ lamella is equal while the 3n order peaks should disappear if $S/P$ volume ratio is 1/2. These are the cases for our samples, PSP-3 and PSP-5, respectively. Figure 3 shows the electron micrographs for PSP/PDP blend with different $S/P$ ratio. Again lamellar structures were observed for both PSP-3/PDP-3 ($\phi_s=0.5$) and PSP-9/PDP-2 ($\phi_s=0.33$) as was shown in Figure 1. Here it was checked that basic mitrodomain structures were conserved by blending labeled and unlabeled block copolymers with almost the same composition and chain lengths.

Incoherent-subtracted and circular-averaged SANS intensities obtained from through view measurements for PSP-3/PDP-3 and PSP-9/PDP-2 are plotted against the wave vector in Figure 4 and their Guinier plot are shown in Figure 5. From the slopes of these plots we estimated the radius of gyration, $R_g$, of polystyrene chains along the direction parallel to the domain interface and those values are compared in Table III. In this table, $R_g, x/R_g, x_0$ values are also
listed, these values express the "contraction factor" of the block chain along the direction parallel to domain interface where $R_g x_0$ denotes the unperturbed radius of gyration reduced to one-dimension. Comparing the $R_g x / R_g x_0$ ratios for PSP-3/PDP-3 and PSP-9/PDP, the value for the former is larger than the latter beyond experimental errors. Even if we consider the difference in molecular weight of polystyrene part, this comparison is still meaningful.

These results lead us the following conclusion. As we mentioned before, the center block, polystyrene have to have either loop or bridge conformation in microdomain structures. It can safely be assumed that $R_g x$ for a block with loop-type conformation is larger than that with bridge-type conformation if they have the same molecular weight. Applying this assumption to our present data, we may consider that the center block chains of PSP-9/PDP-2 have bridge-type rich conformation than PSP-3/PDP-3. This conformation for PSP-9/PDP-2, whose P:S:P ratio is 1:1:1, is in accordance with that of B block in ABC three component triblock copolymers, since they form three-phase four-layer lamellar structure when A:B:C=1:1:1\textsuperscript{13}.

**Acknowledgment** This work was financially supported by a grant from the Daiko Foundation and Y. Matsushita would like to express his thanks for their support. The authors also thank Mr. T. Watanabe and M. H. Choshi for their kind help during the sample preparation experiments.
References

    (1972).
CHAIN CONFORMATIONS OF THE COMPONENT POLYMERS AND THE MICROPHASE SEPARATION STRUCTURES OF HOMOPOLYMER/BLOCK COPOLYMER BLENDS

Naoya TORIKAI,*Yasuhiro MOGI,*Yushu MATSUSHITA,*Ichiro NODA and*Charles C. HAN

*Department of Applied Chemistry, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-01 Japan

*Materials Science and Engineering Laboratory,
National Institute of Standards and Technology,
Gaithersburg, MD 20899, U.S.A.

ABSTRACT

Microdomain spacings of lamellar structures formed by styrene homopolymer/styrene-2-vinylpyridine diblock copolymer/2-vinylpyridine homopolymer blends were measured by small-angle X-ray scattering (SAXS) and single chain conformations of block copolymers in the same blend system were measured by small-angle neutron scattering (SANS). The molecular weight of diblock copolymers is 78K-72K, and three kinds of styrene homopolymer (SH) and 2-vinylpyridine homopolymer (PH) pairs were blended, their molecular weight ratios to that of host block chains were 0.17, 0.38, and 0.78, respectively. Two blend ratios of homopolymer (H)/block copolymer (B), i.e. 1/2 and 1/1 were examined. It was found that the domain spacings of all blends are larger than that of pure block copolymer and that they are increasing with increasing the molecular weight of homopolymers and/or with increasing the volume fraction of homopolymers. Further, block chains in the blends were confirmed to have almost the same chain dimension as that of block chain in pure block copolymer system in the direction parallel to the domain interface irrespective of molecular weight and volume fraction of homopolymers.
INTRODUCTION

Microphase separation structures of block copolymers have been well studied with respect to AB diblock copolymers. Among several familiar structures, that is, spherical, cylindrical and lamellar structures, studies on alternating lamellar were particularly well-established and this structure has been understood at the molecular level.\textsuperscript{1)-7)} In short, microdomain spacing $D$ increases with almost two-third power of the molecular weight,\textsuperscript{1)-4)} whereas the block chain is elongated toward the direction perpendicular to the lamellar interface,\textsuperscript{5),6)} while it shrinks toward the transverse direction so as not to change its volume.\textsuperscript{5)-7)}

Recently microphase separation structures from block copolymer/homopolymer blend system has been studied both experimentally and theoretically. Tanaka et al. studied the morphology of S/SI/I system in detail\textsuperscript{8),9)} where S and I denote for polystyrene and polyisoprene. Matsushita et al. have examined the degree of localization of a homopolymer\textsuperscript{10)} and also measured the chain dimension of homopolymers\textsuperscript{11)} for S/SP system, where S and P denote for polystyrene and poly(2-vinylpyridine). Alternatively, Whitmore and Noolandi\textsuperscript{12)} predicted the phase diagram for several blend system.

In this work we focused on studying the chain conformation of block copolymers of block copolymer/homopolymer blends in bulk in combining with the studies on microphase separation structure themselves. To study the chain conformations of block copolymers by SANS, in principle, particular attention should be paid on the "contrast matching" procedure as pointed out by Quan and Koberstein.\textsuperscript{13)} Therefore two-kinds of contrast-match, that is, "phase match" and "composition match" were taken into account in preparing samples. Samples with alternating lamellar structures were used because this structure is geometrically the simplest one and can be conceived as thermodynamically equilibrium structure than others.

EXPERIMENTAL SECTION

Styrene-2-vinylpyrididine (SP) and deuterated styrene-2-vinylpyrididine (DP) diblock copolymers and both component homopolymers (RMS for polystyrene and VPK for poly(2-vinylpyridine)) used in this study were all prepared by an anionic polymerization with cumyl-potassium as an initiator in THF at -78°C.\textsuperscript{14)} The molecular characteristics of the block copolymers and homopolymers are listed in Table I, II, respectively. As shown in Table I, the volume fractions of polystyrene block of block copolymer, $\Phi_S$, for SP and DP were all designed to be around 0.5 so as for polymers to have lamellar structures. Three pairs of RMS and VPK having almost the same molecular weight were prepared. RMS contain 11 wt% styrene-\textsuperscript{d8} segments to match the
The scattering length of styrene homopolymer with that of polymer P. The molecular weight ratios of homopolymers to the corresponding block chain, $M_H/M_B$, are 0.17, 0.38, 0.78.

The blend ratio 11/89 by weight in terms of D/H ratio was chosen for each DP/SP diblock copolymer mixture, since the scattering length of polystyrene mixture matches with that of P at this weight ratio.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$M_n \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
<th>$\Phi_S^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP-77</td>
<td>77.72</td>
<td>1.02</td>
<td>0.53</td>
</tr>
<tr>
<td>DP-77</td>
<td>92.75</td>
<td>1.09</td>
<td>0.50</td>
</tr>
</tbody>
</table>

$a$ $\Phi_S$ are the volume fractions of polystyrene determined by elemental analysis.

<table>
<thead>
<tr>
<th>Blend Code</th>
<th>Sample Code</th>
<th>$M_n \times 10^{-3}$</th>
<th>$M_w/M_n$</th>
<th>$M_H/M_B^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>RMS-3</td>
<td>13</td>
<td>1.08</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>VPK-17</td>
<td>14</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>RMS-4</td>
<td>30</td>
<td>1.02</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>VPK-14</td>
<td>29</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>RMS-5</td>
<td>61</td>
<td>1.02</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>VPK-18</td>
<td>54</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

$a$ $M_H/M_B$ are the molecular weight ratios of homopolymer to block chain.

The same amount of RMS and VPK were blended with these copolymer mixtures and their H/B ratios were 1/2 and 1/1. The film specimens of these mixtures for measurements were prepared by solvent casting from dilute solution of THF. After the films were dried in vacuum, they were further annealed at about 120°C for a week in order to remove the nonequilibrium factor during solvent casting.

Small-angle X-ray scattering (SAXS) measurements were performed at room temperature with a Kratky U-slit camera from the Anton Paar Co., the details of the experimental conditions were described in a previous paper.  

Small-angle neutron scattering (SANS) measurements were carried out at room temperature with a SANS spectrometer at the National Institute of Standards and Technology with a two-dimensional position-sensitive detector.  

The wavelength, $\lambda$, was 9.0Å, and the width of the distribution, $\Delta \lambda/\lambda$, was 0.25. The sample-to-detector distance was 8m. Since it was confirmed that the lamellae are predominantly oriented along the direction parallel to a film surface in previous studies, the scattering intensities for SAXS were obtained from edge views to determine domain spacings, while SANS measurements were carried out only for through view to measure the single chain conformation since essentially no contribution from domain scattering was observed in this view, thus contrast-match has not checked in this study. The edge and through views are defined here as the measurements in which an incident beam are irradiated from the direction parallel and perpendicular to the film surface, respectively. Scattering intensities obtained from SANS through view measurements on the two-dimensional detector.
were circularly averaged at equal q values. Here q is the magnitude of scattering vector defined by $q = (4\pi/\lambda) \sin \theta$ where $\theta$ is the scattering angle.

RESULTS AND DISCUSSION

Figure 1 shows SAXS edge view profiles for blends of which H/B ratio is 1/1. It is clear from this figure that all the profiles exhibit the integral number order peaks but even number order peaks are missing. This is the typical feature in a diffraction pattern from lamellar structures whose thicknesses of two adjacent lamellae are equal. It also shows that the peak positions tend to shift to lower q with increasing the molecular weight of homopolymers mixed. The domain spacing (D) of lamellar structure was evaluated by applying the Bragg's condition $D = 2\pi n/q_m$ to odd number order peaks, where $q_m$ is the magnitude of scattering vector at peak position and n is the odd number.

Domain spacings D evaluated and their ratios relative to $D_0$, which is for the pure diblock copolymer, were listed in Table III. This table shows that the domain spacings are increasing with the molecular weight and the volume fraction of homopolymers.

Here we assumed two extreme models of solubilization of homopolymers into microdomain formed by block chain to consider the mixing manner.

Two models were simply illustrated in Figure 2. The first one is the case in which homopolymers perfectly localize at the center of microdomain formed by diblock copolymers as shown in Figure 2b. In this case it can be assumed that the distance between the chemical junctions on the lamellar interface does not change by blending of homopolymers, that is, $a_{1L} = a_{10}$ where $a_{10}$ is for pure diblock copolymers. Therefore lamellar microdomains are expanded only along

![Figure 1. SAXS edge view profiles for homopolymer/block copolymer. The volume ratio of H/B is 1/1.](image)

<table>
<thead>
<tr>
<th>Blend Code</th>
<th>H/B=1/2</th>
<th>H/B=1/1</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$D/D_0=1.37$</td>
<td>999</td>
</tr>
<tr>
<td>(M1/M2=0.17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>$D/D_0=1.20$</td>
<td>1087</td>
</tr>
<tr>
<td>(M1/M2=0.38)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>$D/D_0=1.58$</td>
<td>1156</td>
</tr>
<tr>
<td>(M1/M2=0.78)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^b$ H/B are homopolymer/block copolymer volume ratio.
the direction perpendicular to the interface, \( D_L > D_0 \) without changing the conformation of block chains. The domain spacing (\( D_L \)) of blend is simply expressed as

\[
D_L = D_0/(1-x)
\]  

(1)

where \( D_0 \) is the domain spacing for pure diblock copolymer and \( x \) is the volume fraction of homopolymers in the corresponding microdomain. The second one is the case in which a homopolymer uniformly solubilizes into the microdomain as shown in Figure 2c. In this case lamellar microdomains are longitudinally and laterally expanded, i.e., \( D_U > D_0 \), \( a_{ju} > a_{jo} \). \( D_U \) values can be estimated by using the relation

\[
D_U = D_0/(1-x)^{1/3}
\]  

(2)

Figure 2. Schematic illustration of two extreme models of solubilization of homopolymers into the microdomain for H/B blends: (a) pure block copolymer (b) perfect localization model (c) uniform solubilization model.

Figure 3 shows the comparison of calculated \( D/D_0 \) for two extreme models and the experimentally obtained values. This figure shows that all experimental data stay in the region between two calculated curves, but the experimental points decrease with decreasing the molecular weight of homopolymers and they approaches \( D_U/D_0 \) curve rather than \( D_L/D_0 \) curve. This implies that the
solubilization manner of homopolymers in microdomain depends on the molecular weight of homopolymers.

**Figure 3.** Comparison between calculated $D/D_0$ for two extreme models and the experimentally obtained values: (---) eq 1; (----) eq 2.

**Figure 4.** Guinier plots of the scattering intensities obtained from SANS through view measurements. Sample II blends ($M_{f}/M_{0}=0.38$ $H/B=1/1$).

SANS measurements were carried out only for through view as mentioned before. After the incoherent scattering intensities were subtracted, the radius of gyration along the direction parallel to the lamellar interface, $R_{g,x}$, for block chain were evaluated. Figure 4 shows an example of Guinier plot of these blends. $R_{g,x}$ was evaluated from the initial slope shown in the figure. Table IV summarizes $R_{g,x}$ of block chain in each blend and the ratios to the unperturbed radii of gyration for block chain, $R_{g,x}/R_{g,x0}$. Here the unperturbed radius of gyration for polystyrene along the direction parallel to the interface, $R_{g,x0}$, was evaluated by $R_{g,x0}=0.163M_{0}^{1/2}(\AA)^{6}$.

Table IV shows that the ratios, $R_{g,x}/R_{g,x0}$, for all blends are nearly equal each other irrespective of the molecular weight and the composition of homopolymers and they are pretty close to the values for pure block copolymer blend. This implies that block chains in the blends are deformed to the same extent as the deformation of pure diblock copolymer chains in bulk even when the distance between adjacent junction points is longer than that of pure block blends.

<table>
<thead>
<tr>
<th>Blend Code</th>
<th>$H/B=1/2$</th>
<th>$H/B=1/1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>38.2±0.9</td>
<td>(0.84±0.02) a</td>
</tr>
<tr>
<td>(Mf/M0=0.17)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>38.6±0.8</td>
<td>39.4±0.8</td>
</tr>
<tr>
<td>(Mf/M0=0.38)</td>
<td>(0.85±0.02) b</td>
<td>(0.87±0.02) a</td>
</tr>
<tr>
<td>III</td>
<td>39.1±0.9</td>
<td>(0.86±0.02) a</td>
</tr>
<tr>
<td>(Mf/M0=0.78)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Numbers in parentheses are $R_{g,x}$ ratios relative to the unperturbed block chain, $R_{g,x}/R_{g,x0}$.
References

2) E. Helfand Macromolecules 8, 552(1975).
10) Y. Matsushita, Y. Mogi, K. Mori, N. Torikai, I. Noda, C. C. Han to be submitted.
11) Y. Matsushita, Y. Mogi, K. Mori, I. Noda, C. C. Han to be submitted.
NEUTRON DIFFRACTION STUDIES OF MOLTEN TL- AND BI-SE ALLOYS

*Takeshi USUKI, *Yoshiyuki SHIRAKAWA, **Sigeru TAMAKI,
†Masanori INUI, †Shin’ichi TAKEDA,
†Kazumasa SUGIYAMA and †Yoshio WASEDA

*Graduate School of Science and Technology,
Niigata University, Niigata 950-21 Japan

**Department of Physics, Faculty of Science,
Niigata University, Niigata 950-21 Japan

†College of General Education,
Kyushu University, Fukuoka 810 Japan

†Institute for Advanced Materials Processing,
Tohoku University, Sendai 980 Japan

ABSTRACT

Neutron diffraction studies on the molten Tl-Se and Bi-Se systems have been carried out over the wide concentration range. Profiles of the total structure factors or the pair distribution functions of both systems are essentially similar to those of pure liquid metals in metal-rich range, suggesting that the additional Se atoms are almost substituted with the metal atoms and they might form a certain short range order, because of the difference in the electronegativities of the constituents. The Bi-Bi configuration which close to that of pure liquid Bi still remains in the Se-rich range. The existence of covalent-type Se polymeric structure is recognized in Se-rich composition range on the molten Tl-Se system. We have also derived the partial structure factors, using three different total structure factors in a small concentration range, where the partial structure factors were assumed to be constant.

INTRODUCTION

The electronic properties of both molten Tl- and Bi-Se systems have been extensively investigated. For example, molten Tl-Se system shows an anomalous behaviour at the stoichiometric composition Tl₂Se which has low electrical conductivity (σ ~ 10Ω⁻¹cm⁻¹ at 500°C) and the large thermoelectric power.¹ In contrast with
the molten Tl-Se system, the molten Bi-Se system has a rather larger electrical conductivity than the critical value of the Mott's criterion on the electron localization ($\sigma \sim 1100 \Omega^{-1} \text{cm}^{-1}$ at $740^\circ\text{C}$). According to their magnetic susceptibility results, it has postulated that an anomaly in the susceptibility isotherm around the stoichiometric composition is exhibited by the formation of local order in the liquid state. However, under the present situation, the bonding nature between unlike atoms in these alloys seems less clear.

The main purpose of this paper is to describe the results of neutron scattering intensities over the wide concentration range and to establish an atomistic configuration of both molten Tl- and Bi-Se alloys in detail.

**EXPERIMENTAL PROCEDURE**

The samples made from 99.99% purity of Tl, 99.99% of Bi and 99.999% of Se were sealed in a cylindrical glass container under vacuum. Neutron beams with the wavelength of $\lambda = 1.0$ Å for the Tl-Se alloys and $\lambda = 1.099$ Å for the Bi-Se alloys were used in the diffractometer of Institute of Solid State Physics (PANSI and 4G), The University of Tokyo at JRR2 and 3 (JAERI). The essential arrangements of the experiment and the correction procedures for the neutron intensity measurements were almost identical to those described in a previous work, although the small angle data are corrected by the measurement with the same size of vanadium rod.

**RESULTS AND DISCUSSIONS**

After applying usual data processing for the absorptions, the net scattering intensities are normalized to evaluate the total structure factor $S(Q)$, where $Q = 4\pi \sin(\theta)/\lambda$. The total error in the structure factors obtained in this work was estimated to be at most 2.0%, thus the error bars in $S(Q)$ are of the order of 0.02 around the first peak position. The total pair distribution function (PDF) $g(r)$ can be written in the following form,

$$g(r) = 1 + \frac{1}{2\pi^{2}r\rho_{0}} \int_{0}^{\infty} Q[S(Q) - 1] \sin(Qr) dQ$$

where $\rho_{0}$ is the average number density of atoms of the sample.

1. **Structure of molten Tl-Se alloys**

   The $S(Q)$s and $g(r)$s for the molten Tl-Se alloys are shown in Figs. 1(a) and 1(b), respectively. The distance between neighbouring atoms in molten Tl$_2$Se (3.12Å) is shorter than that in the crystalline state (3.35Å). This shows that the bonding of Tl-Se pairs is much more covalent compared with that in the crystalline compound. The liquid structure at this composition, however, may be considered to have a short-range order (SRO) characteristic of crystalline Tl$_2$Se. In the Tl-rich range ($x > 0.667$), the structural functions of alloys are almost the same as that of pure liquid Tl. The first peak position of $g(r)$ decreases gradually from 3.31 Å for pure Tl to 3.12 Å for molten Tl$_2$Se,
and the coordination number decreases from 8.45 to 6.09 with the addition of Se. These facts suggest that Se atoms substitute for the Tl atoms and the atomic arrangement varies from metallic to ionic with addition of Se atoms in this range. Therefore, it is suggested that since excess Tl atoms may behave as metallic, the alloys are in a metallic state as seen in the literature of electronic properties.\textsuperscript{1,3}

Fig. 1(a) Total structure factors of molten Tl-Se alloys together with those reported by Kameda \textit{et al.}\textsuperscript{6} (dotted line). (b) Total pair distribution functions of molten Tl-Se alloys.

Fig. 2 Schematic pictures for molten Tl-Se alloys in the Se-rich region. Short lines and long ones in the figure indicate the covalent and ionic bonds, respectively.
Over the entire Se-rich range \((x < 0.667)\), new peaks in \(g(r)\) appear around 2.32 and 3.74 Å. These positions correspond to those of the first two nearest neighbor distances in pure liquid Se. The differences in the peak positions are very small but these peaks disappear rapidly with addition of Tl. In contrast, a peak located around 3.25 Å which is close to the interatomic distance of the Tl-Se bond in the crystalline Tl₂Se increases with the addition of Tl. These effects may be attributable to an appearance of the strong Tl-Se bonding and the break-up of the polymeric liquid Se structure as illustrated schematically in Fig. 2. The more ionic character of the bonding in this concentration range may induce an increase in the electrical conductivity.

In order to understand more completely the SRO and bonding nature between Tl and Se atoms in molten Tl-Se system, it will be required to determine separately three partial structural functions. It seems to be a valid assumption that each partial structure is approximately independent of the relative abundance of the constituent elements in the alloys if the change in \(S(Q)\) is gradual.⁹ Although these partial structural functions may involve some ambiguity due to the inevitable errors in the separation procedure, their derivations should be important to see more about the local configuration. The partial structure factors were calculated by solving the simultaneous equations and then the best fit values of \(S_{ij}(Q)\)'s were determined by a least square analysis. The calculation of the partial PDF, \(g_{ij}(r)\), was made by the usual Fourier transformation.

---

Fig. 3(a) Three partial pair distribution functions of Tl₀.₆₆₇Se₀.₃₃₃. (b) Three partial pair distribution functions of Tl₀.₄Se₀.₆.
The partial PDF, $g_{ij}(r)$, for molten Tl-Se alloys centered at 66.7 and 40 at.% Tl content are given in Figs. 3(a) and 3(b), respectively. In the Tl-rich region, the partial structures of like atom pairs are close to that of pure liquid Tl with slight broadening. This seems to indicate that, in spite of the appearance of ionic bonds with addition of Se atoms, the partial structure of Tl-Tl pairs depends scarcely on the composition and that the Se atoms simply replace with Tl ones. On the other hand, in the Se-rich region, the partial structure of Se-Se pairs is close to that of the pure liquid Se. The nearest neighbour distance of unlike atom pairs is located at 3.25 Å. This position corresponds to that of the first nearest neighbour distance in crystalline Tl₂Se. This seems to indicate that the bonding nature of Se-Se pairs is covalent and that of Tl-Se pairs is ionic.

2. Structure of liquid Bi-Se alloys

The $S(Q)$s and $g(r)$s for the molten Bi-Se alloys are shown in Figs. 4(a) and 4(b), respectively. The structural profile of liquid 85 at.% Bi alloys is found to agree well with that of pure liquid Bi. The first peak position of $g(r)$ decreases linearly from 3.33 Å for pure liquid Bi to 2.87 Å for molten Bi₂Se₃ and the coordination number decreases rapidly from 8.0 to 4.1 with increasing Se content. Contrary, the humps located at about 4.15 Å increases with increasing Se content. These facts suggest that Se atoms in the Bi-rich range replace with Bi atoms in the liquid state, and with increasing Se content there forms smoothly a short range order which is related to that in crystalline

Fig. 4(a) Total structure factors of molten Bi-Se alloys together with those reported by Satow et al. (dotted line). (b) Total pair distribution functions of molten Bi-Se alloys.
Bi$_2$Se$_3$. Therefore, in the Bi-rich range, Bi atoms may behave as metallic so that the alloys have a metallic character as seen in the literatures on electronic properties. With increasing Se content toward the stoichiometric composition (Bi$_2$Se$_3$), the atomic arrangement in the alloys indicates a nonmetallic character. These features may be more evident in what follows.

According to the hard-sphere model, the hard-sphere structure factor for simple liquid metals shows that a ratio ($Q_2/Q_1$) of the position of the second peak ($Q_2$) to that of the first peak ($Q_1$) is about 1.86. The ratio ($Q_2/Q_1$) is much larger for Bi, ($Q_2/Q_1$)=2.0. On increasing Se content, the deviation from the simple liquid metal is even more remarkable (the ratio for Bi$_2$Se$_3$ is 2.16). These effects are attributable to the appearance of strong Bi-Se bonding and a decrease of the metallic liquid Bi structure as stressed before. Thereafter an increase in ionic bonding part for Se-rich range may induce a decrease in the electrical conductivity.

Figure 5 shows $g_{ij}(r)$ of the molten Bi-Se alloys together with the corresponding line expression $g_{ij}^{\text{cryst}}$ of the crystalline Bi$_2$Se$_3$. Since the $g_{\text{Se-\text{Se}}}$ is in fair to agreement with the $g_{\text{Se-\text{Se}}}^{\text{cryst}}$, no existence of Se polymeric structure is confirmed in the whole concentration range presently investigated. The first peak position of the $g_{\text{Bi-\text{Se}}}$ is also found to agree with that of the $g_{\text{Bi-\text{Se}}}^{\text{cryst}}$. This seems that the crystalline Bi$_2$Se$_3$-like configuration of Bi-Se pairs remains to some extent in the liquid state, which actually observed before. It is of interest that the profile of $g_{\text{Bi-\text{Bi}}}$ is close to that of pure liquid Bi with a slight shortening of the peak positions, rather than to the $g_{\text{Bi-\text{Bi}}}^{\text{cryst}}$. This seems to indicate that the Bi-Bi configuration which is not far from the pure liquid Bi still remains in the liquid structure, in spite of the appearance of the strong Bi-Se bonds with increasing Se content. Because of these features, we consider that the peak positions of $g_{\text{Bi-\text{Se}}}$ are appreciably shifted expect for the first peak.

![Fig. 5 Three partial pair distribution functions of molten Bi-Se alloys.](image-url)
Studies of the single crystals in the region of solid solution for Bi – Bi$_2$Se$_3$ lead to a conclusion that the various ordered structures occur which are made up of five-layer Bi$_2$Se$_3$ type units and two-layer Bi$_2$ units. For example, the layer sequence for Bi$_8$Se$_9$ is [(Bi$_2$Se$_3$)$_3$ – Bi$_2$]$_3$, (Bi$_2$Se$_3$)$_2$ – Bi$_2$ for BiSe, (Bi$_2$Se$_3$ – Bi$_2$)$_3$ for Bi$_4$Se$_3$ and so on. Consequently, it is inferred that there are two distinct local atomic configurations, i.e., one is the Bi-Se ionic configuration and the other is the Bi-Bi configuration, are inhomogeneously mixed in the liquid state.

In conclusion, it is inferred that the change of local atomic structure at the stoichiometric composition might cause the composition dependences observed in the electronic properties such as the metal-nonmetal transition.

ACKNOWLEDGMENTS

Authors express their thanks to The Institute of Solid State Physics, The University of Tokyo, for providing us to use the diffractometer (PANSI and 4G).

REFERENCES

NEUTRON DIFFRACTION OF MOLten NOBLE METAL HALIDES.

* Yoshiyuki SHIRAKAWA, *Takeshi USUKI, *Shigeru TAMAKI, †Masanori INUI,
  ‡Shin'ichi TAKEDA, ‡Kazumasa SUGIYAMA and ‡Yoshio WASEDA.

* Graduate School of Science and Technology,
  Niigata University,
  Ikarashi, Niigata-shi, Niigata-ken, 950-21 Japan

* Department of Physics, Faculty of Science,
  Niigata University,
  Ikarashi, Niigata-shi, Niigata-ken, 950-21 Japan

† College of General Education,
  Kyushu University,
  Ropponmatsu, Chuō-ku, Fukuoka-shi, Fukuoka-ken, 810 Japan

‡ Institute for Advanced Materials Processing,
  Tohoku University,
  Katahira, Aoba-ku, Sendai-shi, Miyagi-ken, 980 Japan

ABSTRACT

Neutron diffraction experiments have been applied for molten CuCl-CuBr and
AgBr-Agl system along the liquidus curve. For molten CuClₓBr₁₋ₓ mixtures,
the contraction of the interionic distance are found at x=0.25 and 0.75. These
results are consistent with those found in the magnetic susceptibilities for
this system. Molten AgBrₓI₁₋ₓ mixture shows an expansion of the interionic
distance in their concentration dependence.

INTRODUCTION

The determination of structure factors by neutron diffraction method is one of the
main important experiments in the study of molten salts. From the diffraction exper-
miments, CuCl and CuBr have tetrahedral coordination in solid and liquid phase, and
exhibit a partially covalent bonding nature¹,²,³. It is remarkable that the results of
magnetic susceptibility⁴ for this system show an anomalous deviation from weidemann

© 1995 Academic Press
rule. Crystalline AgBr have the rock salt type structure as well as most of alkali halides which are the typical ionic matter. On the other hand, AgI is superionic compound from 147°C to melting point, and it is reflected from covalency in chemical bonding. Hence molten CuCl₂Br₁₋ₓ and AgBr₂I₁₋ₓ are interesting system in view of chemical bonding and local configuration. This prompts us to carry out the neutron diffraction experiments in varying the concentration systematically.

**EXPERIMENTAL PROCEDURE**

The samples in this diffraction measurements were sealed in a quartz tube of inner diameter 12.5mm with 1.5mm wall thickness under vacuum of $10^{-4}$ Torr.

Neutron diffraction experiments were carried out using the two axis diffractometer of Institute of Solid State Physics (PANSI and 4G), The University of Tokyo at the high flux reactor of JRR-2 and JRR-3. Reflection from a pyrolitic graphite crystal as used to select a beam with wave length $\lambda = 1.11\text{Å}$ for molten AgBr-AgI and $\lambda = 1.00\text{Å}$ for molten CuCl-CuBr system from the reactor neutron spectrum.

In a typical experimental run, counts were taken at 1.0° intervals for 4.0° ($2\theta$), 11.0°, at 0.5° intervals for 12.0° ($2\theta$), 43.5°, at 1.0° intervals for 44.0° ($2\theta$), 81.0° and at 2.0° intervals for 83.0° ($2\theta$), 105.0°.

Measured temperature in molten AgBrₓAgI₁₋ₓ system is 540°C for $x = 0.9$, 470°C for $x = 0.75$, 530°C for $x = 0.6$ and 630°C for $x = 0.2$. In molten CuClₓBr₁₋ₓ, measured temperature is 620°C for $x = 0.75$, 630°C for $x = 0.5$, 650°C for $x = 0.25$ and 620°C for $x = 0.1$.

The angle dependence were corrected by using the measurement of a vanadium rod. The basic arrangements and correction procedures of measured intensity data were almost identical to those employed in previous work. The experimental uncertainty in the present structural information can be estimated as follows. The accumulated intensity counts are about 2.0×10⁴ in the first peak region. Based on the detailed discussion for systematic error analysis in neutron diffraction by North et al., the total error in the structure factor obtain in this work was estimated to be at most 2.0%.

**EXPERIMENTAL RESULTS**

The total structure factors $S(q)$ for molten AgBrₓI₁₋ₓ, referred molten AgBr at 580°C and AgI at 660°C are shown in Fig. 1. The profile of $S(q)$ in molten AgBr₀.9I₀.1 is similar to molten AgBr except for a growth at about 3.0Å⁻¹. $S(q)$ for molten AgBr₀.2I₀.8 have the same behaviour compared with that of molten AgI. But the profiles molten AgBr₀.75I₀.25 and AgBr₀.95I₀.04 are different from those of molten AgBr or AgI. Their first peaks of $S(q)$ are about 2.5Å⁻¹ and larger than the other. These may imply that molten AgBrₓI₁₋ₓ have a different configuration from molten AgBr and AgI, or at least they are not an ideal mixture of molten AgBr and AgI. In addition, the molten AgBrₓI₁₋ₓ mixtures have a larger pre-peak at about 1.0Å⁻¹ compared to those in molten AgBr and AgI. The pre-peak may indicate an chemical order.

The total structure factors $S(q)$ for molten CuClₓBr₁₋ₓ are shown in Fig. 1, comparing with those of molten CuCl at 505°C and CuBr at 480°C. These $S(q)$ vary systemati-
cally with changing concentration. But S(q) of these mixture have a larger pre-peak than molten CuCl and CuBr.

Fig. 1: The total structure factors of molten CuCl$_x$ CuBr$_{1-x}$ and AgBr$_x$ AgI$_{1-x}$.

DISCUSSION

The total pair distribution functions $g(r)$ can be written in the following form,

$$g(r) = 1 + \frac{1}{2 \pi^2 r \rho} \int_0^\infty \{S(q) - 1\} q \sin(qr) dq$$

where $\rho_0$ is the averaged number density of atoms of sample. The calculated $g(r)$'s of molten AgBr-AgI system are shown in Fig. 2. The second peaks of all $g(r)$ are the different profile from molten AgBr and AgI. The first peak position with varying the concentration of anions are shown in Fig. 3. The change of the first peak position corresponds to that of interionic distance. As seen in Fig. 3, the interionic distance expands where this maximum is at about $x = 0.3$. Magnetic susceptibilities of molten AgBr-AgI system vary linearly with the composition at 600°C$^8)$. Therefore the expansion of interionic distance in this system occurs without a change of chemical bond.

The total pair distribution functions of molten CuCl-CuBr system are shown in Fig. 2. Figure 3 shows the concentration dependence of the first peak position. This curve deviates from the linear change, and have minima at $x = 0.25$ and $x = 0.75$. They
indicate contractions, corresponding to the results of magnetic susceptibilities. Therefore the contraction may be caused by a change of the valence electron distribution.

Molten AgI and cuprous halides have a tetrahedral coordination which reflected the pre-peak of their \( S(q) \) at low \( q \) region. In order to estimate the size of the tetrahedron, the pre-peak fitted by Lorentzian are carried out the Fourier transform about molten CuI and AgI. Results are shown in Fig. 4. The first peaks are 4.41Å for molten CuI and 4.44Å for molten AgI, respectively. Hence both molten CuCl-MBr\(_{1-x}\) and AgBr\(_{1-x}\) systems have some size contributions which are reflected pre-peak of \( S(q) \).

![Graphs showing pair distribution functions](image)

Fig. 2: The total pair distribution functions of molten CuCl\(_{x}\)CuBr\(_{1-x}\) and AgBr\(_{x}\)AgI\(_{1-x}\).

**CONCLUSION**

Molten pseudo binary systems of CuCl-CuBr and AgBr-AgI are not ideal mixture in their concentration dependence of two different anions. But these two system exhibit much different behaviours. One shows the expansion of the interionic distance, and another has the contraction. This fact indicates that the valence electron contribution in a ligand field with the change of anion. While the properties of molten CuCl-CuBr mixture, which are similar in their ionicities, are reflected from the anion size effect, the difference of ionicities between AgBr and AgI may affect to the behaviours in the molten AgBr-AgI system.
A more detailed interpretation and a more quantitative discussion for molten CuCl-CuBr and AgBr-AgI will be described in the subsequent paper.

![Graphs showing concentration dependence of first peak position of g(r) for molten CuCl-CuBr and AgBr-AgI.](image)

**Fig. 3:** The concentration dependence of the first peak position of $g(r)$ for molten CuCl-CuBr$_{1-x}$ and AgBr$_x$AgI$_{1-x}$.

![Graphs showing g(r) for molten CuI and AgI.](image)

**Fig. 4:** Contributions of the pre-peak in the low $q$ region of molten CuI at 665°C and AgI at 665°C.
REFERENCES


Vesicle Formation in the Block Copolymer/Homopolymer Mixture Studied by Scattering Methods

Satoshi Koizumi, Hirokazu Hasegawa, Junich Suzuki and Takeji Hashimoto
Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan
*Department of Physics, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

Abstract

We studied morphology and spatial segmental distribution of particular binary mixtures of poly(styrene-block-isoprene)-(SI) and homopolystyrene, either protonated (HS) or deuterated (DS), with small angle X-ray scattering (SAXS) and neutron scattering (SANS). The block copolymer SI used itself had a lamellar microdomain. Molecular weights of HS and DS were identical to each other and equal also to that of polystyrene block (PS) in SI. SAXS results obtained for SI and HS mixtures show that: (1) HS is solubilized in the PS microdomains; (2) the polysioprene lamella has the thickness independent of $w_{HS}$, weight fraction of HS, but its undulation depends on $w_{HS}$. These two findings, in turn, imply that the HS added is localized in the middle of the PS microdomains, i.e., in between the PS brushes emanating from the interface of SI. We further confirmed this implication by SANS with a deuterium labeling technique; the DS segments studied for the SI/DS mixture is localized in the middle of PS microdomain with the penetration depth of 10 nm between DS and PS block chains.

Introduction

Self-assembled structures in the solvent-cast films of binary mixtures of poly(styrene-block-isoprene)-(SI) and protonated homopolystyrene (HS) were studied as a function of $r_s$, the ratio of molecular weights of HS and polystyrene block in SI as well as function of $w_{HS}$, the weight fraction of HS. For $r_s < 1$ (the criterion for "wet brush"), HS tends to be solubilized into the microdomain of polystyrene (PS) and to swell the PS chains, causing a change of microdomain morphology with long range order. Spherical microdomains composed of polysioprene (PI) block dispersed randomly in the matrix of HS and PS ("spherical micelles") are formed at the limit of high $w_{HS}$ ($w_{HS} ightarrow 1$). For $r_s > 1$ (the criterion for "dry brush"), HS tends either to be segregated from SI, forming a macrophase-separated morphology (at $r_s >> 1$), or to be solubilized into the PS microdomains without swelling PS or without a significant change of a degree of swelling with $w_{HS}$, if any, (at $r_s \approx 1$) (see Figure 1 for possible states of A-B/A mixtures). In the latter case, HS dose not significantly affect the lamellar microdomains of PI for particular SI studied here, which by itself gives an alternating lamellar microdomains of PS and PI, but increases the mean distance between them. As $w_{HS} \rightarrow 1$, the long range spatial order of the PI lamellae is lost, while keeping their thicknesses constant and uniform, resulting in the morphologies of lamellar, cylindrical, and spherical vesicles. The vesicular morphology was analyzed by small-angle X-ray
scattering and transmission electron microscopy. At \( r_s >> 1 \) (still in the criterion of "dry brush"), SI and HS undergo macrophase separation, forming the SI domains composed of alternating lamellae in the matrix of HS. In this paper, we will focus on the mixture in the dry brush criterion of \( r_s = 1 \) and discuss the self-assembled structures formed in such a system by scattering technique (SAXS and SANS) and by the real space observation of transmission electron microscopy (TEM). It should be mentioned that the concept of the wet and dry brush in block copolymer/homopolymer mixtures is the attractive problem and a number of theoretical and experimental studies have been reported \( 5,6,7,8 \).

Figure 1  The schematic diagram of the possible structures for A-B/A mixture.

**Experimental Section**

**Sample Specimens**

Protonated homopoly-styrene HS coded S62 and deuterated homopoly-styrene DS coded SD63 were prepared by living anionic polymerization. SI block copolymer (H102) prepared also by living anionic polymerization was kindly supplied by Kurare Co., Ltd. The characterization of these polymers are summarized in Table 1. It is important to note that S62 and SD63 have almost identical degree of polymerization. All film specimens were prepared by casting method with Toluene which is neutrally good solvent for both PS and PI. The solvent was evaporated slowly over 10 days at 30 C. The film specimens of 0.5 mm thickness thus prepared were annealed in a vacuum oven at 130 - 150 C for two hours to avoid the non-equilibrium effect of solvent-cast as much as possible.

**Electron microscopy**

The self-assembled patterns obtained in the film specimens were examined by TEM using ultra-thin section of ca. 50 nm thickness stained with osmium tetroxide (OsO4) vapor. The PI phase is selectively stained by OsO4 and appears dark in the electron micrographs, while the unstained PS phase appears bright.

**Small-angle X-ray scattering**

The self-assembled patterns were investigated also by SAXS. The SAXS profiles in the direction normal to the film surfaces were obtained with the incident beam of parallel to the film surfaces (edge configuration). The SAXS profiles were corrected for air scattering, absorption and thermal diffuse background scattering (TDS).

**Small-angle neutron scattering**

For the binary mixtures H102/SD63, SANS measurement has been done with an instrument JRR-3 at Japan Atomic Energy Research Institute (JAERI) in Tokai. The scattering data collected with a two dimensional detector were sector-averaged and corrected for air scattering, absorption and incoherent background scattering. In this experiment, film specimens were stacked side by side into a sheet with their film normals perpendicular to both
the propagation direction of the incident neutron beam (x-axis) and vertical axis of the apparatus (z-axis); the thickness along x-axis is 1 mm.

**TEM experimental results**

Figure 2 shows electron micrographs obtained from the binary mixtures of H102/S62. In the micrographs, dark parts correspond to PI rich domains stained with osmium tetroxide and bright parts correspond to HS rich domains. Neat H102 formed alternating lamellar microdomains, as expected for nearly equal volume fraction of PS and PI. For the mixtures of H102/S62, HS was selectively solubilized into the PS lamellar microdomains expanding the interlamellar distance. Macroscopic segregation of S62 was not observed for all binary mixtures studied here and block copolymer H102 keep forming the lamellar microdomains dispersed in the matrix of HS independently of \( w_{HS} \). No morphological transition was observed with increasing \( w_{HS} \), indicating that a penetration depth of HS into the brush formed by PS block chains, which causes the asymmetry in the effective volume fraction between a PS block chain and a PI block chain, is very small and the dry brush was formed between the PS block chains and HS. The HS localized in the center of PS phase screens out the interaction between PS block chains emanating from the opposite SI interfaces and therefore each PI bilayer tends to bend independently in the HS matrix. The electron micrographs show clearly that the degree of bending of PI bilayers increases with \( w_{HS} \).

**SAXS experimental results**

In Figure 3, relative intensities of SAXS for the binary mixtures H102/S62 with various \( w_{HS} \) are plotted as a function of scattering vector \( q = (4\pi/\lambda)\sin(\theta/2) \), \( \lambda \) being the wavelength of the incident X-ray (\( \lambda = 0.154 \) nm). The SAXS profile for neat H102 is typical of the lamellar microdomains with a long-range spatial order, showing scattering maxima up to, at least, the 10th order at integer multiples of the first order maximum. For the mixtures having \( w_{HS} < 0.3 \), as \( w_{HS} \) increases, the scattering maxima arising from interlamellar interference shift toward smaller q and at the same time the intensity of higher-order maxima are suppressed. Both changes result from the selective solubilization of HS into the PS lamellar phase without macrophase separation. The shift of maxima is due to the expansion of interlamellar spacing D and the suppression of higher order maxima is due to the broadening of the distribution of D. For the mixtures having \( w_{HS} > 0.3 \), the broad maxima appeared instead of the sharp maxima, because of the suppression of interlamellar interference in higher q region. These
broad maxima originate from the intraparticle interference and in this case, particles corresponds to isolated lamellae of the PI bimolecular layers. It should be noted that the positions of these broad maxima are at constant q vectors, independent of w_HS. This result implies that there was no morphological transition in the system having w_HS > 0.3 and the thickness of the PI bimolecular layer is kept constant with increasing w_HS. Some minor changes were observed for the mixtures having w_HS > 0.7: the third-order maximum arising from the intralamellar interference becomes broader and the slope of profiles becomes steeper in higher q region (q > 1.5 nm⁻¹). These results will be discussed in detail later.

Figure 4 shows the dependence of the interlamellar distance and the thickness of the PI bimolecular layer on φ_HS, volume fraction of HS, estimated by SAXS. If we assume that added HS solubilized into the PS phase completely and the mixture forms the dry brush system, we can obtain the following formula predicting the change of interlamellar distance as a function of φ_HS:

\[
D(φ_{HS}) = D_0/(1-φ_{HS})
\]  

where \(D_0\) is the interlamellar distance for neat H102. The solid curve in Figure 4 is drawn by eq.(1). Experimental interlamellar distance are somewhat smaller than the values expected by eq. (1). This result indicates that the HS and PS chains satisfy closely the dry brush criterion. The dry brush criterion is also confirmed by the fact that the thickness of the PI bimolecular layer \(D_{PI}\) is constant and independent of \(φ_{HS}\).

**SANS experimental results**

In order to study the spatial distribution of homopolymer using SANS, we used SD63 instead of S62: we prepared the binary mixture H102/SD63 having the composition of (30/70). Figure 5 shows two dimensional SANS patterns for the binary mixture H102/SD63 (30/70) at room temperature with the camera length, \(l = 1.5\) m and the wavelength of neutron, \(\lambda = 0.41\) nm. It should be noted that lamellar microdomains tend to be oriented preferentially with their interfaces parallel to the free surface of the cast-films. It is clearly seen that the pattern (a) focused on the high intensity level in the low q region.
shows strong anisotropic scattering oriented in the horizontal direction, while the pattern (b) focused on the low intensity level in the high q region (0.35<q<2 nm⁻¹) shows a circularly symmetric intensity distribution around the incident beam.

Figure 6 shows the SANS profiles obtained by sector-averaging over azimuthal angle, μ, from 20 to 20 for the binary mixture H102/SD63 (30/70). The q region shown in Figure 6 was covered with the following two experimental setups, l= 1.5 m, λ = 0.41 nm as well as l=10m, λ = 0.63 nm. The relative intensity thus obtained is plotted double-logarithmically as a function of q. Here we defined the crossover scattering vector q_c marked by an arrow in Figure 6. For q < q_c, the scattering intensity drops rapidly with the slope of ca. -6, while for q > q_c, the scattering intensity drops gradually with the slope of ca. -2. It should be noted that the scattering in q < q_c corresponds to that the anisotropic pattern shown in Figure 5 (a), while the scattering in q > q_c corresponds to that attributed to the isotropic pattern shown in Figure 5 (b). The details will be discussed in the next section.

Analysis and Discussion

The Characteristic Parameters estimated by SAXS

The corrected SAXS profiles reflect the spatial distribution of the PI segments or of PI lamellae. The theoretical scattering profiles based on the one-dimensional paracrystal model⁹,¹⁰ were first smeared for the slit height and width and best-fitted to the experimental ones to obtain the characteristic parameters describing the phase structure. The characteristic parameters obtained are the interlamellar distance D, the thickness of the PI bimolecular layer D_P1, the distribution of the thickness of the PI bimolecular layer σ_P1, the characteristic interfacial thickness between PS and PI t₁, the volume fraction PI layer Φ_P1,SAKS ≡ D_P1/D which are summarized in Table 2.

<table>
<thead>
<tr>
<th>Specimen Composition</th>
<th>D (nm)</th>
<th>D_P1 (nm)</th>
<th>σ_P1 (nm)</th>
<th>t₁ (nm)</th>
<th>g</th>
<th>Φ_P1</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>61.0</td>
<td>32.0</td>
<td>1.2</td>
<td>2.0</td>
<td>0.01</td>
<td>0.525</td>
</tr>
<tr>
<td>80/20</td>
<td>70.5</td>
<td>30.5</td>
<td>1.2</td>
<td>2.0</td>
<td>0.03</td>
<td>0.433</td>
</tr>
<tr>
<td>70/30</td>
<td>77.5</td>
<td>30.5</td>
<td>1.2</td>
<td>2.0</td>
<td>0.06</td>
<td>0.394</td>
</tr>
<tr>
<td>60/40</td>
<td>95.0</td>
<td>30.5</td>
<td>1.2</td>
<td>2.0</td>
<td>0.10</td>
<td>0.321</td>
</tr>
<tr>
<td>50/50</td>
<td>115.0</td>
<td>29.9</td>
<td>1.5</td>
<td>2.0</td>
<td>—</td>
<td>0.260</td>
</tr>
<tr>
<td>40/60</td>
<td>—</td>
<td>29.5</td>
<td>1.5</td>
<td>2.0</td>
<td>—</td>
<td>0.224</td>
</tr>
<tr>
<td>30/70</td>
<td>—</td>
<td>30.4</td>
<td>1.5</td>
<td>2.5</td>
<td>—</td>
<td>0.169</td>
</tr>
<tr>
<td>20/80</td>
<td>—</td>
<td>30.5</td>
<td>1.7</td>
<td>2.5</td>
<td>—</td>
<td>0.114</td>
</tr>
</tbody>
</table>

Table 2 The Characteristic parameters for H102/S62 mixtures.

Scaled Structure Factor obtained by SAXS

For the SAXS measurement, the phase structure formed by SI is described by a two phase lamellar model. The SAXS intensity I(q) from isolated lamellae of thickness D_P1 with a certain orientation distribution in 3-D space is given by

I(q;D_P1) = Φ_P1Δρ^2 D_P1τ^2 sin^2(qD_P1/2)/(qD_P1/2)^2

(2)

where Δρ is the difference in electron densities between the PI lamellae and the matrix phase, and A is the area of the flat part of the interface, A = ξ^2 where ξ is the persistence length of the interface. Defining

D_P1 = π/q_m

(3)
where \( q_m \) is the value of \( q \) at the first order maximum from isolated lamellae, one obtains

\[
I(q)q^2q_m \sim \Phi_P A \Delta \rho^2 S(y)
\]

(4)

with the scaled structure factor given by

\[
S(y) = (\sin y/y)^2
\]

(5)

and

\[
y = (\pi/2)(q/q_m)
\]

(6)

Figure 7 shows the scaled scattered intensity \( I(q)q^2q_m = 1(x)x^2q_m^3 \) plotted double-logarithmically with the scaled scattering vector \( x=q/q_m \) for the H102/S62 mixtures with \( w_{HS} \geq 0.4 \). The scaled structure factors are found to be universal with \( \Phi_{HS} \) or with \( w_{HS} \) up to 0.6. Upon further increase in \( w_{HS} \) the structure factor changes slightly, in a manner that the scattering maxima, especially higher order ones, become broader.

The intensity rapidly drops for \( q/q_m > 3 \) due to the increase in \( \sigma_{PI} \) and \( t_1 \), which is related to the screening of the interaction between neighboring lamella.

**Scattering Intensity obtained by SANS**

Based on the two dimensional SANS patterns shown in Figure 5, the scattering intensity, \( I_{d}(q) \), for \( q < q_c \) originates from the phase structure associated with the lamellar microdomains which are highly oriented with their interfaces parallel to the film specimens. On the other hand, the scattering intensity, \( I_{I}(q) \), for \( q > q_c \) originates from the thermal concentration fluctuations of DS and PS in the microphase composed of DS and PS. In the strong segregation limit, we note that the added DS (SD63) is selectively solubilized into the PS microphase, but not into the PI microdomains. This solubilization induces the penetration of DS into the brush formed by the PS block chains, giving rise to the concentration fluctuation and thus \( I_{I}(q) \) because of the contrast between protonated and deuterated segments.

Therefore total elastic scattering intensity, \( I_{total}(q) \), from our system may be described by the following formula

\[
I_{total}(q) = I_{d}(q) + I_{I}(q)
\]

(7)

In the context of the mean field random phase approximation (RPA), \( I_{I}(q) \) may be approximated by

\[
I_{I}(q) \sim 1/\Phi_1 g(q,R_g_1) + 1/\Phi_2 g(q,R_g_2) - 2 \chi
\]

(8)

\[
g(q,R_g_i) = 2N_i/(qR_g_i)^2[(qR_g_i)^2 + \exp((qR_g_i)^2) - 1]
\]

(9)

with \( R_g_i = N_i\alpha^2/6 \),

where \( g(q,R_g_i) \) is the Debye function, \( \chi \) is the Flory interaction parameter between HS and DS which is negligibly small, \( R_g_i \) is the radius of gyration of \( i \)-th polymer, "\( \alpha \)" is the statistical segment length and \( \Phi_i \) is the volume fraction of PS or DS on the polystyrene
microdomain. Since the polymerization indices for HS and DS are nearly equal to each other, \( N = N_1 = N_2 \),

\[
I_d(q) \sim \Phi_1 (1 - \Phi_1) g(q; R_g) \tag{10}
\]

In order to describe the elastic scattering for the phase structure, we must consider the three-phase lamellar model which are characterized by the two thicknesses of layers, \( D_1 \) and \( D_2 \), shown in Figure 8 (Figure 8 schematically shows the spatial distribution of scattering length normal to the lamellar interface). In this case, \( D_1 \) corresponds to the thickness of the bimolecular layer formed by the block copolymer and \( D_2 \) corresponds to the thickness of the polyisoprene bilayer, \( D_{PI} \). In the mixtures having high \( w_{HS} \), the lamellar vesicles formed by SI are isolated in the matrix of DS. The interfaces between PI block and PS block and that between PS block and DS have finite characteristic interfacial thicknesses. The spatial variation of the scattering length for such a system can be described by a convolution product of the step function, characterizing the systems with sharp interfaces, and Gaussian smoothing functions with standard deviations, \( \sigma_1 \) and \( \sigma_2 \), characterizing the interfacial widths. The one-dimensional fourier transform of this model, \( F(q) \), is given as follows.

\[
F(q) \sim \Delta B_1 \left[ \sin(D_1 q/2) / (D_1 q/2) \right] \exp(-\sigma_1^2 q^2/2) \\
+ \Delta B_2 \left[ \sin(D_2 q/2) / (D_2 q/2) \right] \exp(-\sigma_2^2 q^2/2) \tag{11}
\]

where \( \Delta B_1 \) is the difference in scattering length between PS and DS and \( \Delta B_2 \) is the difference in scattering length between HS and PI. The characteristic thickness of the interface, \( t_i \) is defined by

\[
t_i = (2\pi)^{1/2} \sigma_i \quad (i = 1 \text{ or } 2). \tag{12}
\]

Our system has the special condition, \( \Delta B_1 >> \Delta B_2 \). Under this condition, \( F(q) \) becomes equal to that for the simple two phase model given by

\[
F(q) \sim \Delta B_1 \left[ \sin(D_1 q/2) / (D_1 q/2) \right] \exp(-\sigma_1^2 q^2/2) \tag{13}
\]

Eq.(13) was used to analyze the phase structure of our system. In the \( q \) range satisfying \( q > 1/D \), \( D \) being the repeat distance of the DS phases predicted by eq.(1), the lattice factor (or interference function between the DS phases) for \( I_d(q) \) becomes unity, as the distance \( D \) has large fluctuation for high \( w_{HS} \). Our system satisfies this criterion, since \( L = 200 \text{ nm} \) and \( q \) range studied is \( 0.1 < q < 2.0 \) (nm\(^{-1}\)). Therefore \( I_d(q) \) is given in terms of the independent scattering function of the DS domains, i.e.,

\[
I_d(q; D_1) \sim q^{-2} F(q)^2 \\
\sim q^{-2} \left\{ \Delta B_1 \left[ \sin(D_1 q/2) / (D_1 q/2) \right] \exp(-\sigma_1^2 q^2/2) \right\}^2 \\
\sim q^{-2} \exp(-\sigma_1^2 q^2) \tag{14-a}
\]

or

\[
\ln\{I_d(q)^4\} = (\text{const}) - \sigma_1^2 q^2 \tag{14-b}
\]

where the additional factor, \( q^{-2} \), is the Lorentz factor for the lamellar systems having an orientation distribution in 3-D space and their lateral dimensions much greater than their lamellar thickness, \( D_1 \).

**Penetration depth estimated by SANS**

We tried to analyze the parameter \( \sigma_1 \) characterizing the penetration depth of DS at PS/DS interface on the basis of
For this purpose we first separate the two contributions $I_d(q)$ and $I_t(q)$ to the observed net scattering $I_{\text{total}}(q)$ in eq.(7). We estimated $I_t(q)$ by fitting the theoretical function given by eq.(10) to the experimental profile $I_{\text{total}}(q)$ at $q > q_c$ with $R_g$ as an adjustable parameter. The best fit obtained with $R_g = 7$ nm gives the scattering function for $I_t(q)$ as shown by the broken line in Figure 6. The scattering function for the phase structure $I_d(q)$ is obtained by subtracting the fitted function from the experimental data $I_{\text{total}}(q)$ based on eq.(7). The subtracted scattering profile which corresponds to the scattering function of the phase structure is also plotted with square symbol in Figure 6. This scattering function $I_d(q)$ originates from the bimolecular layer of block copolymers of thickness $D_1$ and the interfacial thickness $t_{11}$ between DS and PS. On the grounds that the scaled structure factor obtained by SAXS is universal with $w_{HS}$ in this $q$ region and have close to $q^{-4}$ dependence, the deviation of the SANS intensity $I_d(q)$ from $q^{-4}$ behavior is due to the finite interfacial thickness between PS and DS. Figure 9 shows the plots to evaluate the value $\sigma_1$ from which the values of $t_{11}$ are determined using eq.(12). The $q$ region used to evaluate $\sigma$ is $0.03 < q < 0.15$ which is lower than $q_c^2$. The evaluated values, $\sigma_1$ and $t_{11}$ are 4.5 and 11.4 nm respectively. The interface between PS and DS is broader than that between PS and PI block but is very close to the radius of gyration of polystyrene block chains.

![Figure 7 The schematic diagram of the spatial distribution of the difference of scattering length for H102/SD63 (30/70).](image7)

Figure 6 SANS profile for H102/SD63.

![Figure 8 Porod plot. ln(I(q)q^4) vs. q^2.](image8)

Figure 8 Porod plot. ln(I(q)q^4) vs. q^2.

**Conclusion**

Self-assembly of the binary mixtures of the lamellar SI and HS observed in films obtained by solution-cast and subsequent annealing was investigated as a function of $w_{HS}$ under a special condition $r_5=1$ where the PS block chains behave as a "dry brush". The PI microdomains keep the lamellar structure with a uniform thickness in the matrix of HS or
DS, despite of increases in the interlamellar distance D and its distribution $\sigma_D$ caused by the increase in $w_H$. However, as D increases, the lamellae tend to undulate at a length scale greater than the persistence length $\xi$, because of the screening of the interaction between PI block chains emanating from the opposing interfaces. The penetration depth of DS into the PS brush was about 10 nm by using SANS technique.

References

INVERSION OF THE PHASE DIAGRAM IN POLYMER BLENDS STUDIED BY SMALL-ANGLE NEUTRON SCATTERING

*Hiroshi JINNAI, *Hirokazu HASEGAWA, *Takeji HASHIMOTO and *Charles C. HAN

*Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

*Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

ABSTRACT

The miscibility of an amorphous mixture of normal (protonated) polybutadien (HPB) and perdeuterated polybutadiene (DPB) has been extensively studied and was characterized by an upper critical solution temperature (UCST). In this study the miscibility of HPB and DPB as a function of temperature was studied by small-angle neutron scattering (SANS). The vinyl component of the DPB was held constant at 16%, while the vinyl fraction of the HPB was varied from 17-80%. The binary interaction parameter, $\chi$, was obtained. The mixtures of DPB and HPB with 17-39% vinyl show UCST behaviors; i.e., $\chi$ increases with decreasing temperature. The mixture of DPB and HPB with 52% vinyl was found to have almost no temperature dependence. However, the mixture of DPB and HPB with 65-80% show a lower critical solution temperature (LCST) behavior; i.e, $\chi$ increases with increasing temperature. This inversion of the phase diagram from UCST to LCST has never been observed.

INTRODUCTION

Binary blends of rubbers (polydienes) are widely used in the rubber industry to tailor the properties to the application. However, little is known about how to control the miscibility of rubber blends, the knowledge of which would be important to make materials with better properties. Small-angle neutron scattering (SANS) is a powerful method to examine the concentration fluctuations present in polymer blends in the single-phase state.

Recently, the miscibility of amorphous mixtures of normal (protonated) and perdeuterated polybutadiene (hereafter referred to as HPB and DPB, respectively) has been extensively studied as a model system; it was characterized to have a phase diagram with an upper critical solution temperature (UCST) by the use of SANS technique.\textsuperscript{1,3} Bates et al.\textsuperscript{2,3} studied such an isotope polymer blend and explained the origin of partial miscibility in terms of the reduction in carbon-hydrogen bond length resulting from substituting deuterium for hydrogen (isotope effect). For the DPB/HPB blend, however, since polybutadiene consists of 1,2-units (vinyl) and 1,4-units (see Figure 1), the microstructure in the blend should be another important factor affecting the miscibility of the blend. Note that 1,2-unit and 1,4-unit of DPB can be obtained with the substitution of deuterium for hydrogen in the figure. Sakurai et al.\textsuperscript{1} separated out the isotope effect and the microstructure effect through a systematic SANS study on DPB/HPB blends with various vinyl contents on the basis of the theory of random copolymer mixtures.\textsuperscript{4,6} Sakurai et al.\textsuperscript{1} regarded the DPB/HPB blend as a blend of A-B random
copolymers (A and B are the 1.2-unit and the 1.4-unit for DPB, respectively) and C-D random copolymers (C and D are the 1.2-unit and the 1.4-unit for HPB, respectively) and showed that the main contribution to miscibility for the blend is due to the intramolecular pairs of A/B and C/D rather than the isotope pairs of A/C and B/D. These intramolecular interactions account for their observation of negative \( \chi \)'s (\( \chi \) is the binary interaction parameter) for one of their DPB/HPB blend pairs, while only positive \( \chi \)'s are expected for the isotope effect. Therefore, it is extremely important to clarify the effect of the microstructure on the miscibility of the DPB/HPB blends.

In this paper we present experimental evidence of a spin inversion of the phase diagram from UCST to LCST (lower critical solution temperature) with an increase of the vinyl content of HPB, while that of DPB is held constant. Again, this type of phenomenon can never be predicted by merely taking the isotope effect into consideration, implying the importance of the microstructure effect in understanding the miscibility of the DPB/HPB blends.

**EXPERIMENTAL**

Figure 1. Schematic illustration of the chemical structures existing in HPB

One DPB (coded as H2O) and five HPB were synthesized by living anionic polymerization. Table I summarizes the detailed polymer characteristics. In Table I, the sample code (e.g., 17PB91) comprises the vinyl content in \% (first number 17 in this case), polybutadiene (PB), and the weight-average molecular weight, \( M_w \), in units of 1000 (the second number 91 in this case).

<table>
<thead>
<tr>
<th>Table I. Polymer Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Code</td>
</tr>
<tr>
<td>H2O (DPB)</td>
</tr>
<tr>
<td>17PB91 (HPB)</td>
</tr>
<tr>
<td>39PB91 (HPB)</td>
</tr>
<tr>
<td>52PB215 (HPB)</td>
</tr>
<tr>
<td>65PB104 (HPB)</td>
</tr>
<tr>
<td>80PB110 (HPB)</td>
</tr>
</tbody>
</table>

Blend specimens were prepared by dissolving the polymer mixtures with a composition of 30 wt % DPB and 70 wt % HPB in toluene and then casting into films. Five blend specimens with different compositions were prepared in order to examine the phase diagram for the H20/80PB110 system. The as-cast films thus obtained were further dried under vacuum at room temperature until constant weight was attained. The thin as-cast films were pressed into a cell and then carefully degassed in order to avoid bubble formation during heating experiments. The specimens were sandwiched between two oxygen free copper disks and mounted in a heating block. Small angle neutron scattering (SANS) experiments were carried out using the 8-m SANS instrument at the NIST Cold Neutron Research Facility. In this study, pinhole collimation was used with a 9-Å neutron wavelength (\( \lambda \)). The absolute scattering intensity for each specimen was obtained as a function of the wave vector \( q (q = (4\pi/\lambda) \sin (\theta/2); \theta \) being
the scattering angle) by use of a dry silica gel as a secondary standard. A copper heating block was used to control the specimen within ±0.2 °C of the desired temperature.

RESULTS AND DISCUSSION

de Gennes has calculated the structure factor, \( S(q) \), for a binary polymeric blend in the single phase state, in the context of the mean-field model and the random phase approximation (RPA). We used the extended version of the RPA calculation of de Gennes for a system having a molecular weight polydispersity given by the Schultz-Zimm distribution. The structure factor, \( S(q) \), of this version is given by

\[
\frac{k_N}{S(q)} = \frac{1}{\phi_A \langle Z_A \rangle_n v_A S_A(q)} + \frac{1}{\phi_B \langle Z_B \rangle_n v_B S_B(q)} - \frac{2\chi}{v_0}
\]

with

\[
k_N = N_A \left( \frac{a_A}{v_A} - \frac{a_B}{v_B} \right)^2
\]

and

\[
S_i(q) = \frac{2}{X_i^2} \left[ \left( \frac{h_i}{h_i + X_i} \right)^{h_i} - 1 + X_i \right]
\]

where

\[
X_i = q^2 \langle R_{gi}^2 \rangle_n = q^2 \langle Z_i \rangle_n b_i^{2/3}
\]

and

\[
h_i = \left( \langle Z_i \rangle_n / \langle Z_i \rangle_n - 1 \right)^{-1} \quad i = A \text{ or } B
\]

\( \langle Z_i \rangle_n \) and \( \langle Z_i \rangle_w \) denote respectively the number- and weight-average degree of polymerization for the ith component (\( i = A \) or \( B \)), and \( \phi_i \) is the volume fraction of the ith component with molar volume \( v_i \), Kuhn statistical segment length \( b_i \), and neutron scattering length of one monomer unit \( a_i \). \( N_A \) is Avogadro’s number, \( \chi \) is the binary interaction parameter between monomers A and B, and \( v_0 \) is the molar volume of the reference cell defined as

\[
v_0 = (\phi_A / v_A + \phi_B / v_B)^{-1}
\]

The thermal expansion coefficient in the literature \( V^{-1} \partial V / \partial T = 7.5 \times 10^{-4} \text{ K}^{-1} \) was used to estimate the molar volume of DPB and HPB at each measurement temperature. All SANS data were fitted with eq 1 in order to determine \( \chi \) parameters as a function of temperature (T) for each blend. The detailed fitting procedure can be found elsewhere. The error for \( \chi \) was estimated by fitting eq 1 to the data while varying...
the molecular weight of DPB and HPB in the range of ±5% which is an estimated error in the molecular weight measurement. The error for c thus determined was approximately ±1x10⁻⁴ for each measurement.

In Figure 2, χ parameters for five DPB/HPB blends (30/70 wt%/wt%) with different vinyl content of HPB are plotted against the reciprocal absolute temperature (T⁻¹). χ decreases with increasing temperature for the H20/17PB91 blend, suggesting that this blend is a UCST-type mixture. χ also decreases as temperature increases for the H20/39PB91 blend, although the absolute values of the χ parameters are smaller than that for H20/17PB91. It should also be noted that the temperature dependence of χ is weaker for H20/39PB91 than for H20/17PB91. Almost no temperature dependence was observed for the H20/52PB215 blend. We should point out that the χ values of this blend are negative in the temperature range of the experiment. Surprisingly, the temperature dependence of χ is inverted (i.e., χ increases with increasing temperature) for the H20/65PB104 and H20/80PB110 blends, suggesting that these two blends are LCST-type mixtures. It is interesting that the values of χ parameters suddenly become positive again as the vinyl fraction of HPB in DPB/HPB blends increases from 65% to 80%. It should also be emphasized that the temperature dependence of χ for the H20/80PB110 blend is larger than that for the H20/65PB104 blend. This series of χ data for DPB/HPB (30/70 wt% band) blends with a wide range of vinyl content from 17% to 80% in HPB clearly demonstrates the inversion of the phase diagram. To our knowledge, such an inversion of the phase diagram has never been observed. This phenomenon is interesting because one can control not only the extent of miscibility but also the phase separation behavior of DPB/HPB blends by changing the vinyl content of the constituent polymers.

![Graph showing plots of binary interaction parameter, χ, against reciprocal absolute temperature, T⁻¹, for five different DPB/HPB blends.](image)

**Figure 2.** Plots of binary interaction parameter, χ, against reciprocal absolute temperature, T⁻¹, for five different DPB/HPB blends.

SANS measurements were also carried out for the H20/80PB110 blends with five different volume fractions of H20 (DPB) (i.e., ϕH20 = 0.272, 0.370, 0.468, 0.572, and 0.683). χ parameters were determined for all compositions as a function of temperature by the same procedure used above. Although the temperature dependence of χ for H20/80PB110 blends with five different compositions will not be presented in this paper (besides the 30/70 wt%/wt% blend which is shown in Figure 2), it is worth noting that these blends have exactly the same features as H20/80PB110 (30/70 wt% band); i.e., χ increases as the temperature...
increases. The mean-field spinodal temperature, $T_s$, is obtained by extrapolating $\chi$ to its value at the spinodal point, which is given by

$$\chi_s = \frac{v_0}{2} \left( \frac{1}{v_A \phi_A \langle Z_A \rangle_w} + \frac{1}{v_B \phi_B \langle Z_B \rangle_w} \right)$$

$T_s$'s at different compositions are plotted against $\phi_{H2O}$ in Figure 3. Although the error bars due to the uncertainty of extrapolation in $\chi$ are significant, it is obvious that the H2O/80PB110 has an LCST-type phase diagram.

The experimental observation of the inversion of the phase diagram in the DPB/HPB blends can be explained on the basis of the random copolymer theory by ten Brinke et al. This analysis is now underway and will be presented at the symposium.

Balazs et al. discussed the effect of sequence distribution on the miscibility of copolymer/copolymer blends. In their model a parameter was introduced to describe a block, random, or alternating copolymer. In the context of this model one can discuss a mixture of two random copolymers, which could be a possible way to explain our data.

**Figure 3.** Phase diagram for a H2O/80PB110 blend. Spinodal temperatures determined by SANS are shown by filled circles along with error bars. The dashed line in the figure is a visual guide.

**ACKNOWLEDGEMENT**

We are grateful to Nippon Zeon Co. for providing three of the five HPB samples (52PB215, 65PB104, and 80PB110). We also thank Japan Synthetic Rubber Co. for supplying two of the five HPB samples (17PB91 and 39PB91).

**REFERENCES**

SMALL-ANGLE NEUTRON SCATTERING STUDY OF AMORPHOUS SI-TI-C-O FIBERS

Kentaro SUZUYA a, Tomoaki KAMIYAMA b, Yuji ITO c
Kiyohito OKAMURA d and Kenji SUZUKI b

a Booster Synchrotron Utilization Facility
National Laboratory for High Energy Physics
1-1 Oho, Tsukuba-city, Ibaraki-ken, 305 Japan

b Institute for Materials Research
Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai-city, 980 Japan

c Institute for Solid State Physics
University of Tokyo
Roppongi, Minato-ku, Tokyo Japan

d College of Metallurgical Engineering
University of Osaka prefecture
1-1 Gakuen-machi, Sakai-city, Osaka, 591 Japan

ABSTRACT

A small-angle neutron scattering (SANS) study of amorphous Si-Ti-C-O fibers was performed using SANS-U spectrometer at JRR-3. Anisotropically scattered strong intensities were observed in the direction perpendicular to the fiber-axis. These are caused by scattering entities with a well-defined boundary. The size of the scattering entities is considerably large. The measurements were made for the fibers suspended in the air and in D2O solvent and show that the fibers have two kinds of scattering entities, one is concerned in the surface irregularities of the fibers and another is concerned in some fluctuation of the structure of the fibers. The integrated intensity of the surface part of the neutron scattering is stronger than that of the inner part about by 2.7 times.

INTRODUCTION

Si-Ti-C-O fibers which were prepared by the Yajima method1) using polycarbsilane as a precursor have been manufactured on an industrial scale by Ube Industries Ltd. The medium-range structure of the Si-Ti-C-O fibers thus prepared was investigated by a small-angle X-ray scattering (SAXS) technique2). The SAXS profile was attributed to two different type of scattering entities: an anisotropic contribution from long filaments with diameters of hundreds to thousands of Ångströms and an isotropic contribution from β-SiC fine clusters of about a nanometer in diameter. The anisotropic part of the SAXS intensity becomes weak, while the Guinier radius and the average inter-particle distance of β-SiC fine clusters increase largely with raising the heat treatment temperature. A drastic degradation in the tensile strength of the fibers at about 1300°C can be understood in terms of this structural modification.

In this work we tried to reveal the origin of the anisotropic SAXS intensity above mentioned, and made small-angle neutron scattering measurements of the Si-Ti-C-O fiber in the q region extending to q < 0.01 Å⁻¹. We made the measurements for the fiber suspended in...
the air and in D$_2$O solvent respectively, and examined the effect of surface irregularities such as oxide layers on the scattered intensity.

**EXPERIMENTAL METHODS**

Si-Ti-C-O fibers were produced by the pyrolysis of polytitanocarbosilane in a N$_2$ gas atmosphere at 1100°C on an industrial scale by Ube Industries Ltd. The chemical composition of this fiber is shown in table 1.

Small-angle neutron scattering measurements were performed using the small-angle neutron scattering spectrometer SANS-U installed at JRR-3 in the Japan Energy Research Institute. For the present experiment, the wavelength of 5 Å, the incident-neutron dose of 8 mm in diameter and the distance from the sample to the detector 12 meter were used. It covered the q range at least from 0.003 to 0.04 Å$^{-1}$.

All the SANS measurements were performed on the samples whose fiber axes were oriented toward one direction and held at the temperature of 20°C in the atmosphere. One measurement was made for the fibers only, that is, suspended in the air, and the fibers suspended in D$_2$O solvent.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>C</th>
<th>O</th>
<th>Ti</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>32.6 ± 0.3</td>
<td>43.8 ± 0.4</td>
<td>23.2 ± 0.2</td>
<td>0.269 ± 0.004</td>
<td>0.056 ± 0.009</td>
</tr>
</tbody>
</table>

**RESULTS**

An example of the measured intensities of Si-Ti-C-O fibers detected by a two-dimensional position-sensitive proportional counter is shown in figure 1 as an iso-intensity contour map. In this figure the contour lines are not necessarily drawn at same intervals to avoid confusion. The central dip of the map is due to a beam stopper. The fiber axis was set along y-axis. The anisotropically scattered strong intensity was observed in the direction perpendicular to the fiber axis, as observed in the small-angle X-ray scattering measurements $^2$.

After background and normalization corrections, the scattered intensities of relative units were obtained in two directions of the scattering vector q perpendicular and parallel to the fiber axis which correspond to x- and y-axis in figure 1. The origin is the beam center. We obtained the scattered intensities by using the circular integration of the two-dimensional data within a pair of sectors of ± 7.5° about x- or y-axis respectively. Figure 2 shows thus obtained scattered intensities of the fiber in the air $I_1(q)$ and suspended in D$_2$O solvent $I_2(q)$ in the x-direction and that of the fiber in the air in the y-direction. Only the scattered intensity in the x-direction, with the scattering vector perpendicular to the fiber axis, is noticed. The scattered intensity parallel to the fiber axis is negligibly weak.

Both the scattered intensities $I_1(q)$ and $I_2(q)$ in the x-direction decay nearly as $I(q) \sim q^{-4}$ in the q region larger than 0.06 Å$^{-1}$ as shown in figure 3. The Guinier approximation can be recognized to hold only in the narrow q range from 0.003 to 0.005 Å$^{-1}$, and this gives the radius of gyration 540 Å. However, we could not observe the scattered intensities in the q region lower than 0.003 Å$^{-1}$ due to the beam stopper, and so we can only give the value of 540 Å or more as the radius of gyration.
DISCUSSION

In figure 2 we can see a definite difference in the scattered intensities between the fibers suspended in the air and those in D$_2$O solvent. To examine the origin of the scattered intensity of fibers, we tried to decompose the scattered intensity into the inner part $I_F(q)$ of the fiber and the surface part $I_S(q)$

$$I(q) = I_F(q) + I_S(q),$$  \hspace{1cm} (1)

the former being due to the filament structure in the fiber and the latter to the surface roughness. The surface part of the scattered intensity must differ in amplitude between the fibers suspended in the air and those in the D$_2$O solvent, while the inner part must be independent of the surrounding media. Therefore, the difference $\Delta I(q)$ between $I_1(q)$ and $I_2(q)$ can be written by

$$\Delta I(q) = I_1(q) - I_2(q) = I_S(q) - I_S(q),$$  \hspace{1cm} (2)

where $I_S(q)$ is the surface part of the scattered intensity from the fibers in the air and $I_S(q)$ is that of the fibers in the D$_2$O solvent. We introduce a ratio $K$ defined by the relation $K = I_S(q)/I_S(q)$. As the media around the fibers are considered not to bring any changes on the structure factor representing the surface roughness, the ratio $K$ ought to depend only on the difference between the nuclear scattering lengths

$$K = \frac{I_S(q)}{I_S(q)} = \frac{(\Delta \rho)^2}{(\Delta \rho')^2},$$  \hspace{1cm} (3)
where $\Delta \rho$ and $\Delta \rho'$ are the differences in the densities of the nuclear scattering lengths between the fibers and the air and those between the fibers and D$_2$O solvent respectively.

On the assumption that the surface component of the fiber is equal to that of the bulk one that is given by table 1, we obtain $K = 2.558$ using the densities in table 2.

Table 2 Densities of nuclear scattering length

<table>
<thead>
<tr>
<th></th>
<th>density (g/cm$^3$)</th>
<th>$r \times 10^{23}$ fm/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Ti-C-O fiber</td>
<td>2.119</td>
<td>3.918</td>
</tr>
<tr>
<td>D$_2$O (20°C)</td>
<td>1.105</td>
<td>6.365</td>
</tr>
<tr>
<td>air (20°C)</td>
<td>0.001205</td>
<td>0.00427</td>
</tr>
</tbody>
</table>

We obtain two kinds of scattered intensities of the fibers in the air, the surface part $I_S(q)$ and the inner part $I_P(q)$, using the equation

$$\Delta I(q) = I_S(q) \cdot (K - 1)/K.$$  \hspace{1cm} (4)

The result is plotted in figure 3. It shows the following evidences:

1) The observed scattered intensity of the fibers is caused by two kinds of scattering entities, one is the surface boundary and another the inner part of the fibers. The integrated intensity of the surface part is stronger than that of the inner part about by 2.7 times.

2) Both the surface and inner parts of the scattered intensity decay nearly as $I(q) \sim q^{-4}$ in the $q$ region larger than 0.06 Å$^{-1}$.

![Graph showing scattered intensities of fiber, its surface and inner part. (equation (1))](image-url)
CONCLUSION

The anisotropically scattered strong intensity of Si-Ti-C-O fibers was observed in small-angle neutron scattering measurements, in the direction perpendicular to the fiber axis as observed in the small-angle X-ray scattering measurements. The anisotropically scattered intensity decays following the Porod law, that is, the scattering is caused by the scattering entities with a well-defined boundary. The size of the scattering entities is considerably large. The radius of gyration is thought to be 540 Å or more.

The Si-Ti-C-O fibers have two kinds of scattering entities along the fiber axis, one is concerned in the surface irregularities of the fibers and another is concerned in some fluctuation of the structure of the fibers. The integrated intensity of the surface part of the neutron scattering is stronger than that of the inner part about by 2.7 times.

The authors would like to thank T. Yamamura and M. Sato of Ube Industries Ltd. for the sample preparation.

References

Small Angle Neutron Scattering Study of Phase Separation in PMMA/SAN

1Yasuo OHISHI, 2Kazuhiro FUCHIZAKI,
1Akio UEMURA, 2Masao MINOBE, 2Jun-ichi SUZUKI and 2Satoru FUNAHASHI

1Tsukuba Research Laboratory
Sumitomo Chemical Co., Ltd.
Kitahara-6, Tsukuba, Ibaraki-ken, 300-12 Japan

2Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

A time-resolved small angle neutron scattering study has been made by utilizing a new Small Angle Neutron Scattering (SANS) machine installed at JRR-3M to investigate the phase separation kinetics in a polymer alloy, poly(methylmethacrylate)/poly(styrene-co-acrylonitrile). This polymer alloy has a lower critical solution temperature, hence the scattered intensity was measured at the two-phase field after a temperature jump above the phase boundary from themiscible state. By observing the time evolution of scattered intensities, several stages changing phenomena of the spinodal decomposition have been detected. In the early stage the characteristic behavior that the maximum scattered intensity \( I_m \) is increasing with time while the wave number \( Q_m \) giving rise to the maximum intensity is kept constant has been clearly observed. Here \( Q_m \) was found to be equal to \( R_g \) where \( R_g \) is the gyration radius of the polymer chain. It should be emphasized that in addition to this observation we have succeeded in detecting the decomposition process in the very early time. The observed power law in this stage is discussed together with a recent theoretical prediction.

INTRODUCTION

The kinetics of phase transition, ordering and pattern construction in polymer alloys have been studied experimentally by utilizing various microscopic, small angle x-ray or neutron scattering, light scattering and so on, as well as theoretically. The spinodal decomposition is one of typical phenomena of the phase separations in binary mixed materials, which are not only solids but also polymers. The fundamentals of the spinodal decomposition in solids were firmly established by the early 1970s. As for the kinetics in polymer alloys, however, several modifications concerning chain configurations of long macromolecules should be taken into consideration. Recently some attempts have made to understand the kinetics of the spinodal

*present address: Department of Physics, Kyushu University.
decomposition in polymers both from experimental and theoretical sides.

However, it is difficult to investigate experimentally the early stage dynamics of the separation. The ordinary light scattering cannot cover the relevant wave number range. The conventional x-ray and neutron source were too weak to catch up with the progress of the decomposition. Recently, high-brilliant synchrotron radiation sources have made the observation feasible. In fact, dynamical behavior at the early stage of the spinodal decomposition in a polymer alloy by using such an x-ray source has been reported.

In this work, we carried out time-resolved small angle neutron scattering experiments by using a new SANS instrument installed at high-flux reactor JRR-3M in JAERI to inquire the spinodal decomposition in polymer alloy, poly (methylmethacrylate) / poly (styrene-co-acrylonitrile) (PMMA/SAN) partially miscible blends.

EXPERIMENTAL

The time-resolved SANS measurements were performed using a new SANS machine installed at the cold neutron beam port (C3-1; characteristic wavelength is 0.6 nm) in the guide hall adjacent to JRR-3M. The wavelength of incident neutron was monochromated to 0.625 nm by the Velocity Selector (4000 rpm, the wavelength resolution δλ/λ is 11%; made by KFKA), and collimated by aligned pinholes. The neutron detector equipped with this apparatus is a 2-dimensional position sensitive proportional counter (LISO) whose efficient circle diameter is 66 cm. Intensity data were stored in the histo-memories in the detector by dividing data into 128 × 128 pixels, each of which covers 5.19 × 5.33 mm² in the active detector area. These data were then collected and analyzed in VAX Station 3500. Data acquisition system was turned up so as to take one snapshot within at least one second. The capacity of the computer memories allows 99 data of such consecutive snapshots to be stored at once. The distance between sample and detector was chosen to be 7 m or 10 m according to the range of scattering wave number. In these condition, we covered the range of scattering wave number Q, from 3 × 10⁻² to 5 × 10¹ nm⁻¹. It should be stressed that the time resolution in this work is 1 minute, reflecting high-flux of cold neutron source.

PMMA/SAN used in this work has a lower critical solution temperature, i.e., there is two-phase state above the critical temperature. The samples were blended deuterated-PMMA (Mₘ=87500, Mₘ/Mₙ=1.03, Polymer Laboratory Ltd.) with SAN(Mₘ=145200, Mₘ/Mₙ=2.07, AN content 30.3%). Blends at critical mixture were prepared by dissolving both d-PMMA and SAN in tetrahydrofuran at a total concentration of 1 wt%, and precipitating into a sheet of 1 mm thickness at 135°C.

Prior to the time-resolved SANS experiment, we have identified the critical temperature (148°C) of decomposition, by monitoring the SANS intensity, as a point at which the scattering intensity suddenly increased. The time rate of decomposition were controlled by changing the quench depth from the critical temperature. We have performed two different procedures in order to look into carefully the early stage dynamics.

RESULT AND DISCUSSION

The gyration radius Rg of the polymer chain was determined by fitting observed scattering intensities in the one-phase field to the Debye function. The dependence of the gyration radius thus obtained (Rg=8nm) on the polymerization is compatible with the previous
work on PMMA chain$^6$).

Shown in figure 1 is the time evolution of the scattered intensities $I(Q)$ after quenching temperature from miscible state ($110^\circ$C) to two-phase field ($165^\circ$C). Immediately after quenching, we can see the onset of early stage of decomposition (figure 1(a)), in which the maximum intensity $I_m$ is increasing as the decomposition proceeds while its position $Q_m$ remains unmoved. Note that the characteristic wave number ($0.11$ nm$^{-1}$) of the early stage is nearly equal to $R_g^{-1}$. Note also that such a wave number regime could not be accessible to ordinary light scattering study. This early stage is followed by the so-called intermediate stage (figure 1(b)), in which $Q_m$ is gradually decreasing as time goes on. The situation that the decomposition process comprises multi-stage nature is more clearly seen by converting the dependencies of $Q_m$ and $I_m$ on time into log-log form as shown in figure 2. From this plot it is inferred that there seems to exist a new stage (denoted as I) prior to above-mentioned stages (denoted as II and III, respectively).

In order to confirm the presence of a new stage, another experiment was carried out, in which the temperature quench depth was chosen to be relatively small (from $140^\circ$C to $151^\circ$C). Moreover, we chose a different starting temperature from that of previous experiment, because upon taking a lower starting temperature scattering due to phase separation was contaminated even in the one-phase field by quasi-elastic scattering due to a glass phase. (The glass transition point is considered to be around $115^\circ$C.) Overall time variation in separation process was in fact retarded through the reduction of the quench depth.

Figure 3 shows the time evolution of the scattering function in this condition. Here the behavior of the early stage is more clearly seen in figure 3(b) than in figure 1(b). Furthermore, we have succeeded in detecting the scattering in the very early times ($\sim$ 2000 seconds). The time-resolved scattering intensities in this stage are depicted in figure 3(a), in which one can see that the peak is shifted slightly with time towards low $Q$ side. Shown in figure 4 is the log-log plots of $I_m$ and $Q_m$ versus time for this run. On the very early term it is difficult to obtain $I_m$ and
Fig. 3 The time evolution of scattered intensity I(Q) after quenching temperature from 140°C to 151°C. (a) the very early stage, and (b) the early stage.

Q_m with high precision because of the weakness of the scattering intensities. As seen from figure 4, we can expect a power-law behavior of Q_m in this very early stage.

The scaling relations of I_m and Q_m with time (I_m ∼ t^θ, Q_m ∼ t^φ) for each stages are tabulated in Table 1. The ratio of the exponents θ/φ in the intermediate stage was obtained to be 3.4, which is not inconsistent with that obtained for a binary polymer mixture. The magnitude of θ obtained in the very early stage supports the classical Cahn-Hilliard theory rather than the theory recently proposed by Kawasaki and Koga in which hydrodynamic effect is taken into consideration. This is considered to be due large polymerization, which results in weaker coupling of the order parameter field to the convective flow. In other words, a polymer chain is too long for the hydrodynamic effect to become effective. In order to see this effect experimentally in the very early time rather smaller polymerization or shallower quench should be required.

Table 1

<table>
<thead>
<tr>
<th>stage I</th>
<th>stage II</th>
<th>stage III</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ</td>
<td>-0.28 (-0.26)</td>
<td>0.0 (0.0)</td>
</tr>
<tr>
<td>θ</td>
<td>2.09 (1.26)</td>
<td>1.04 (0.99)</td>
</tr>
<tr>
<td>θ / φ</td>
<td>-7.5 (-4.8)</td>
<td>—</td>
</tr>
</tbody>
</table>

Q_m quenched from 140°C to 151°C

Fig. 4 Log-log plot of I_m and Q_m versus time when the temperature is quenched from 140°C to 151°C.

Fig. 5 The scaled scattering function, log (I_m/Q_m) versus log (Q/Q_m). (a) early stage when the temperature was quenched from 140°C to 151°C, (b) intermediate stage when the temperature was quenched from 110°C to 165°C.
Figure 5 shows the log-log plot of the scaled scattering function $I/I_\infty$ versus $Q/Q_\infty$. In the early stage shown in figure 5(a), the width of the scaled function becomes narrower with the progress of the decomposition, i.e., with the increase in the amplitude of concentration fluctuations. In contrast to this behavior, scattering functions in the intermediate stage falls into a single scaling function as shown in figure 5(b). There is a bump at $Q/Q_\infty=4.0$ reflecting the periodicity of the boundary between PMMA and SAN.

CONCLUSION

We have succeeded in detecting the progress of the spinodal decomposition of PMMA/SAN in the very early time stage, i.e., in the length scale of order of tens of nanometers, in addition to rather well-established stages already reported. Emphasis should be laid on the fact that this is nothing but owing to a high cold neutron flux of JRR-3M.

ACKNOWLEDGMENT

The SANS apparatus used was designed by Dr. S. Katano of JAERI. We thank Prof. Y. Amemiya and Dr. T. Kojima, for their technical support about the instrumentation for time-resolved experiments. Two of us (Y.O. and K.F.) thank Prof. K. Kawasaki and Drs. T. Kawakatsu and T. Koga for fruitful discussions.

This work was performed on the co-investigation contract with Japan Atomic Energy Research Institute and Sumitomo Chemical Co., Ltd.

REFERENCES

1) as a review,
2) for example,
3) for example,
LOW-ENERGY MODES AND MEDIUM-RANGE CORRELATED MOTIONS IN PD79Ge21 ALLOY GLASS

Kaoru SHIBATA, Hiroshi MIZUSEKI and Kenji SUZUKI
Institute for Materials Research, Tohoku University
Katahira 2-1-1, Aoba-ku, Sendai 980, JAPAN

ABSTRACT

It is well known that there are excess modes over the sound wave in low energy region below about 10 meV in glass materials, which do not exist in corresponding crystalline materials. We examined the low energy modes in a Pd79Ge21 alloy glass by means of inelastic neutron scattering. Measurements were performed on the crystal analyzer type time-of-flight spectrometer LAM-40 with PG(002) and Ge(311) analyzer mirror, which is installed at KENS. The dynamic structure factor S(Q,ω) was obtained over the wide momentum range from 0.5 to 5.2Å⁻¹. The measured S(Q,ω)'s have almost same momentum(Q) dependence at each energy (ℏω) in the energy range from 2.0 to 8.0 meV. In the energy region below 3 meV, we found a small shoulder peak at Q=1.7Å⁻¹ in the momentum dependence of S(Q,ω). It corresponds to a prepeak in S(Q). Therefore it is concluded that the low energy modes in Pd79Ge21 alloy glass is mainly contributed from medium-range correlated motions in the cluster consisting of a few chemical short-range structure units of Pd6Ge trigonal prism.

INTRODUCTION

Besides the Debye-type harmonic motion, the dynamic structure of glasses is characterized by three different contributions as follows: (1) diffusional relaxation near the glass transition, (2) excess harmonic vibration in low energies of 1-4 meV and (3) tunneling in a two-level system at very low temperatures below 1 K.
The second contribution mentioned above has been often found as an anomalous excess in the specific heat and thermal conductivity appearing around the temperature of 10-50 K, which corresponds to the energy of 1-4 meV. Currently, this low-energy excess excitation is known to be originated from the medium-range motion between fundamental structural units constructing the network structure of glasses such as SiO₂₁ and GeSe₂²).

In this paper we examined the low energy modes in a Pd₇₉Ge₂₁ metal-metalloid alloy glass by means of inelastic neutron scattering and found the origin of these modes; the medium-range correlated motions in the cluster consisting of a few chemical short-range structure units of Pd₆Ge trigonal prism.

EXPERIMENTAL

The Pd₇₉Ge₂₁ alloy glass was prepared in the form of thin ribbons about 2mm in width and less than 30µm in thickness by rapid cooling from the melt using a single roller method. The specimens were sealed in a thin Al cylindrical container with dry He gas. The weight of sample was about 80 g. The container is of 20mm in inner diameter and about 80mm in length.

The neutron scattering experiments were performed on the medium resolution time-of-flight (TOF) spectrometer LAM-40³), which is installed at the KENS pulsed neutron scattering facility (National Laboratory for High Energy Physics, Japan). On the inverted geometry spectrometer, pyrolytic graphite; PG(002) reflection, is normally used as a neutron energy analyzing mirrors. In this mode of operation, the energy resolution is about 150µeV for elastic scattering and the momentum transfer range is from 0.2 to 2.6 Å⁻¹. The LAM-40 spectrometer has another optional set of analyzing mirrors using the Ge(311) reflection. When the Ge mirrors set is used, the energy resolution is about 900µeV for elastic scattering and the momentum transfer range is from 0.4 to 5.1 Å⁻¹. The measurements are carried out at 295K.

RESULTS AND DISCUSSION

The inelastic neutron scattering spectra of Pd₇₉Ge₂₁ glass and Pd₇₅Ge₂₅ crystal are compared around the two positions of Q=1.7 and 2.6 Å⁻¹ in Fig.1 ⁴). The value of Q=1.7 Å⁻¹ corresponds to the position of the
pre-peak in $S(Q)$ and the position of $Q=2.6$ Å$^{-1}$ is closely located near the main peak $Q=2.8$ Å$^{-1}$. An excess intensity is obviously observed for the glass at $Q=1.7$ Å$^{-1}$ with in a low-energy range of $\hbar\omega < 3$ meV, compared with the crystal. Same behavior is also found in the spectrum observed at $Q=2.6$ Å$^{-1}$, but the excess intensity is extended to a high-energy range of $\hbar\omega < 6$ meV.

Fig. 1 Inelastic neutron scattering spectra of Pd$_{79}$Ge$_{21}$ glass and Pd$_{75}$Ge$_{25}$ crystal observed over a low excitation energy range at pre-peak position ($Q=1.7$ Å$^{-1}$) in $S(Q)$ and just below main peak position ($Q=2.6$ Å$^{-1}$) in $S(Q)$. The energy resolution is illustrated at elastic position.

Fig. 2 $Q$-dependence around $Q=1.7$ Å$^{-1}$ (pre-peak marked by arrow) in $S(Q,\omega)$ of Pd$_{79}$Ge$_{21}$ glass for elastic and inelastic scattering in a low excitation energy range of $\hbar\omega < 5$ meV.
Figure 2 shows the $S(Q, \hbar \omega)$ as a function of $Q$ for the elastic scattering integrated over an energy-resolution width of $\hbar \omega = 1.0 - 0.3$ meV and the inelastic scattering intensities integrated over selected energy intervals of $\hbar \omega = 1.5 - 2.5$ and $2.5 - 4.5$ meV, respectively. The pre-peak is clearly found around $Q = 1.7 \ \text{Å}^{-1}$ in the elastic structure factor, but drastically reduced in the inelastic one with increasing $\hbar \omega$. In the range of $\hbar \omega > 5$ meV the pre-peak is totally diminished.

**Fig. 3** (a) The generalized phonon density of states $G(\omega)$ for $\text{Pd}_{79}\text{Ge}_{21}$ glass and $\text{Pd}_{75}\text{Ge}_{25}$ crystal.
(b) the total specific heat of $\text{Pd}_{79}\text{Ge}_{21}$ glass; broken line: the phonon term calculated by the measured $G(\omega)$ for the glass, dashed-and-dotted line: a fitted electron term ($\gamma T$), solid line: the calculated total specific heat and open circle: the measured total specific heat.

In the generalized phonon density of states $G(\hbar \omega)$, an excess intensity is also obviously observed for the glass with in a low-energy range of $\hbar \omega < 7$ meV, compared with the crystal in Fig. 3(a). Figure 3(b) shows a good agreement of the calculated phonon term by the measured $G(\hbar \omega)$ for glass, and the measured specific heat except the electron term in specific heat. The phonon term in specific heat of $\text{Pd}_{79}\text{Ge}_{21}$ glass has a significant excess deviation from the Debye model in a temperature range below 30K, as shown in Fig. 3(b). This temperature range corresponds well to the energy range of $\hbar \omega < 3$ meV, where the excess intensity of neutron inelastic scattering is observed at the $Q$-value of pre-peak.
The pre-peak position of $Q=1.7$ Å$^{-1}$ closely corresponds to the atomic spacing of $r=4$ Å between Ge atoms occupying the central sites in adjacent trigonal prismatic structural units connected by sharing an edge$^5)$, as shown in Fig.4. Therefore, we conclude that the low-energy excitation of $\hbar \omega=1-3$ meV at $Q=1.7$ Å$^{-1}$ existing in Pd$_{79}$Ge$_{21}$ glass, which contributes to an excess specific heat appearing below 30 K in addition to the Debye model, is originated from a hinge-like locally collective motion between trigonal prismatic structural units connected by sharing an edge.

REFERENCES

CRYSTALLIZATION OF Fe$_{75.8}$(Cu, Nb)$_{3.5}$(Si, B)$_{20.7}$ AMORPHOUS ALLOY STUDIED BY SMALL ANGLE NEUTRON SCATTERING

*Ô. OHNUMA, †J. SUZUKI, *Y. USUI, †S. FUNAHASHI and *Y. HAMAGUCHI

*Department of Materials Science and Engineering, M uroran Institute of Technology M uroran, Hokkaido 050, Japan

†Department of Physics, Japan Atomic Energy Research Institute Tokai, Ibaraki 319-11, Japan

Abstract

The crystallization of Fe$_{75.8}$(Cu, Nb)$_{3.5}$(Si, B)$_{20.7}$ amorphous alloy has been studied by small angle neutron scattering in magnetic field. The magnetic contribution of the scattering has been distinguished from the nuclear contribution for alloys with various annealing temperatures and time. The existence of magnetic fluctuation has been confirmed even in amorphous state. The peak corresponding to the correlation between crystallized phase has been found in the Q region of 0.2 ~ 0.3nm$^{-1}$. However, over 0.4nm$^{-1}$ region the scattering function I(Q) decays as Q$^{-2}$ ~ Q$^{-3}$ which are unexpected functions for precipitates with rigid surface, Q$^{-4}$. For the alloys of 500°C 60min and 550°C 60min the contribution of the nuclear scattering can be observed in the region of Q<0.1nm$^{-1}$

Introduction

Fe-Cu-Nb-Si-B alloys called FINEMET are well known materials which have ultra fine grain structures and show excellent soft magnetic properties.\(^1\)\(^-\)\(^3\) These materials can be prepared by the crystallization of amorphous Fe-Cu-Nb-Si-B alloys. For understanding the mechanism of magnetic properties of FINEMET, especially permeability, it is important to get the average microscopic information during the crystallization of these alloys. Small angle neutron scattering(SANS) has the great advantage for this purpose, because neutron has large penetrativeness and interacts with magnetic moment in the materials. In this paper we have measured SANS of Fe$_{75.8}$(Cu, Nb)$_{3.5}$(Si, B)$_{20.7}$ alloy in magnetic field and classified the scattering into the magnetic and the nuclear scattering.
Experimental

Fe_{75.8}(Cu, Nb)_{3.5}(Si, B)_{20.7} amorphous alloy ribbon with 20 mm wide used in this study was kindly provided from Hitachi Metals Ltd.. As-quenched and heat treated samples were prepared for this measurement. The heat treatment has been made at 450°C, 500°C, 550°C for 10 ~ 60 min in nitrogen gas atmosphere. The samples for SANS measurement were cut into 20 mm x 20 mm and stacked up to 12 sheets. The measurement were performed using the small angle neutron scattering spectrometer(SANS-J) installed at the cold neutron source of the JRR-3M in the JAERI. The magnetic field was applied on the sample surface along the direction perpendicular to the incident beam direction.

Results and discussion

Figure 1 shows the SANS profiles of as-quenched sample measured in different magnetic field. The strong scattering is observed in low Q region and the shoulder is also observed at 0.1 nm^{-1} under zero magnetic field. This strong scattering including the shoulder indicates the existence of long range magnetic fluctuation in amorphous state, because this scattering completely disappears in the magnetic field of 0.87 T and reproduces after removing the magnetic field. Comparing the profile in the magnetic field of 0.1T with that of 0.87T, there seems to be no difference between these profiles. This result indicates that the magnetization of the sample is saturated in these magnetic field. In such a saturated state of magnetization, the magnetic scattering contributes just to the profile measured along the direction perpendicular to the magnetic field. Figure 2 shows differential profiles between the profile measured in zero field and the profile measured along the direction perpendicular to the field of 1T. These data include only the information of magnetic fluctuation in amorphous matrix, because the profile perpendicular to the field includes nuclear scattering and the strongest magnetic scattering which remained under the magnetic field. According to TEM observation, the amount of crystallized phase increases in the next order; 450°C 10min, 450°C 60min, 500°C 10min, 500°C 60min, 550°C 60min. The scattering intensity decreases with increasing the amount of crystallized phase up to 500°C 10min, corresponding to decreasing amorphous matrix. However a little increasing of the intensity is found from 500°C 10min to 500°C 60min and there is no difference between 500°C 60min and 550°C 60min which is optimum condition for improving permeability. Figure 3 and 4 show the SANS profiles measured in 1T for the amorphous alloy annealed at several temperatures for 10min and 60min . Scattering profiles I(Q//H) measured along the direction parallel to H shown in the Fig.3, originate from only nuclear scattering. On the other hand, the profiles I(Q.L.H) in which scattering vector Q is perpendicular to H are shown in Fig.4. These profiles include both nuclear and magnetic component. In the region of 0.2<Q<0.3nm^{-1} there is a peak
corresponding to the correlation between crystallized phases in both Fig.3 and Fig.4. The space between precipitates calculated from this peak position is about 20-30nm which coincides with the value obtained by TEM observation. Over 0.4nm\(^{-1}\) region the scattering curves take asymptotic forms of \(I(Q)\propto Q^{-2}\) which are unexpected forms for the precipitates with rigid surface, \(Q^{-4}\). Below 0.1nm\(^{-1}\) region scattering can be found clearly in the profile of 500\(^\circ\)C 60min and 550\(^\circ\)C 60min, in striking contrast to 450\(^\circ\)C 10min and 450\(^\circ\)C 60min in which little scattering is observed. It seems that these scattering mean the existence of the fluctuation in the distribution of precipitates. Figure 5 shows the differential intensity \(I(Q\perp H)-I(Q//H)\), indicating only magnetic scattering. The peak shown in the Fig.4 can be found clearly. The correlation spacing calculated from this peak position is about 30nm and 20nm for the alloy annealed at 450\(^\circ\)C and 500\(^\circ\)C 550\(^\circ\)C, respectively. This length also coincides with the value mentioned above. This coincidence indicates that magnetic moments are mounted in the precipitates dominantly. The ratio of the scattering intensity \(I(Q\perp H)/I(Q//H)\) for the sample annealed at 550\(^\circ\)C for 60min shown in Fig.6. In the range of \(Q>0.4\)nm\(^{-1}\) this ratio almost constant, namely nuclear and magnetic contribution originate from the same microstructure. On the contrary below 0.4nm\(^{-1}\) this value decreases with lowering the scattering vector and approach to 1 which means there is no magnetic contribution in the low \(Q\) region.

Conclusion

The crystallization of Fe\(_{75.8}\)(Cu, Nb)\(_{3.5}\)(Si, B)\(_{20.7}\) amorphous alloy has been studied by SANS in the magnetic field. The magnetic scattering has been distinguished from the nuclear scattering for several alloys with various annealing temperatures and time. The present investigation is the first step to study the crystallization of Fe\(_{75.8}\)(Cu, Nb)\(_{3.5}\)(Si, B)\(_{20.7}\) amorphous alloy by SANS. The construction of the model which can describe the scattering profiles has been in progress.

References

Fig. 1 Magnetic field dependence of SANS profile for an as-quenched sample.

Fig. 2. Differential profiles between the profile measured in zero field and the profile perpendicular to the field of 1T for the samples with various annealing temperatures and time. These data include only the information of magnetic fluctuation in amorphous matrix.
Fig. 3. Scattering profiles I(Q//H) in which scattering vector Q is parallel to H for the samples with various annealing temperatures and time measured in the magnetic field of 1T.
Fig. 4. Scattering profiles $I(Q \perp H)$ in which scattering vector $Q$ is perpendicular to $H$ for the samples with various annealing temperatures and time measured in the magnetic field of 1T.
Fig. 5. The differential profiles, $I(Q \perp H) - I(Q // H)$, for the samples with various annealing temperatures and time measured in the magnetic field of 1 T. These data indicate only magnetic scattering.
Fig. 6. The ratio of the scattering intensity $I(Q_{\perp}H) / I(Q/H)$ for the sample annealed at $550^\circ C$ for 60 min measured in the magnetic field of 1T.
SUPERThermal uCN-PRODUCTION AT JAERI
—ANALYSIS—

"H. M. Shimizu, "T. Kawai and "K. Sakai

"National Laboratory for High Energy Physics, 1-1 Oho, Tsukuba, 305 Japan

"Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun
Osaka, 590-04 Japan

"Bubble Chamber Research Laboratory, Tohoku University, Sendai, 980 Japan

ABSTRACT

The experimental results concerning the production of ultra-cold-neutrons (UCNs) in superfluid helium at 0.45 – 1.5K contained in a stainless-steel tube of 3m long and 8cm diameter was analyzed by a numerical simulation which took into account the non-isotropic momentum distribution. The experimental method to study the momentum distribution and to determine the UCN density in the long tube is discussed.

INTRODUCTION

Ultra-cold-neutron (UCN) is a very good tool for precision measurements of the properties of the neutron. Measurements of the neutron electric-dipole-moment (EDM) has provided the most reliable upper limit to the breaking of the time-reversal-invariance. The technique used to store UCN in a bottle remarkably improved the upper limit of neutron-EDM. UCNs have been produced by gravitational deceleration and turbine deceleration. Golub and Pendlebury 1) proposed to produce UCN by cold-neutron scattering in superfluid 4He (superthermal method). Cold-neutrons of about 9Å were expected to be efficiently converted to UCNs within the framework of single-phonon emission theory. 1) 2)

In 1991, Yoshiki et al. 3) measured the UCN counting rate as a function of the incident cold-neutron wavelength, and confirmed that UCNs are produced at around 9Å. The experimental setup is shown in Fig. 1. UCNs were produced in a superfluid helium at 0.45 – 1.5K contained in a stainless-steel tube 3m long and 8cm diameter, which was placed horizontally (UCN container). The inner surface of the UCN container was electropolished in order to avoid UCN loss by reflection from a rough surface. UCNs were extracted through a 4cm-diameter gravity acceleration tube connected vertically to the UCN container. The extracted UCNs were gravitationally accelerated so that they could penetrate the aluminum window at the bottom of the gravity acceleration tube. The counting rate of the UCNs measured by a neutron counter placed below the gravity acceleration tube was 0.4s\(^{-1}\). In Ref. [3], this value was interpreted as being the UCN
density in the UCN container assuming that the angular distribution of UCN is isotropic in single-phonon emission and it remains isotropic while UCN travels in the UCN container and UCN has a Boltzmann type energy distribution. They obtained a UCN density 1/100 of that calculated based on single-phonon emission theory. However, measurements of the angular and energy distribution are necessary to deduce the UCN density if the counting rate strongly depends on the angular and energy distribution.

Fig. 1 Experimental setup for studying superthermal UCN production carried out at JAERI in 1991.

The determination of the UCN density is important in order to discuss the feasibility of future experiments using our superthermal UCN converter. In this paper, we report on the results of a numerical simulation concerning the relation between UCN density accumulated in the UCN container and the counting rate at the bottom of the gravity acceleration tube, while taking into account the non-isotropic angular distribution.

**NUMERICAL SIMULATION**

A UCN propagation inside the UCN container was numerically simulated by a Monte Carlo simulation. We assumed that UCNs are reflected specularly on the surface of the UCN container. We write the angular distribution of UCNs as \( f(\theta, v) \), where \( \theta \) is the polar angle of the UCN momentum about the incident cold-neutron beam and \( v \) is the velocity of UCN. The \( f(\theta, v) \) is normalized to be

\[
\int d\Omega \int_{v_{\text{max}}}^{v_{\text{max}}} dv f(\theta, v) = 1, \tag{1}
\]
where \( v_{\text{max}} \) is the maximum velocity of UCNs in the UCN container. The counting rate at the bottom of the gravity acceleration tube \((N_0 \text{s}^{-1})\) can be written as

\[
N_0 = n \int d\Omega \int_0^{v_{\text{max}}} dv f(\theta, v) v h_0(\theta),
\]

(2)

where \( n \text{[cm}^{-3}\text{]} \) is the UCN density in the UCN container and \( h_0(\theta) \) is the extraction rate of UCNs traveling at \( v = 1 \text{m/s} \) in the direction of \( \theta \) for \( n = 1 \text{[cm}^{-3}\text{]} \). If we assume that the energy distribution of UCNs obeys the Boltzmann distribution, the function \( f(\theta, v) \) is given as \( f(\theta, v) = 3v^2/4\pi v_{\text{max}}^2 \). The result of an experiment carried out by Yoshiki et al. \(^3\) gives the relation

\[
\frac{3}{4} n v_{\text{max}} \int d\Omega h_0(\theta) = 0.4 \text{s}^{-1}.
\]

(3)

Fig. 2 shows the angular distribution of UCNs with \( v = 5 \text{m/s} \) traveling in the UCN container for 6, 30 and 60s after production. The angular distribution is assumed to be isotropic on the production and the reflectivity of UCN container wall 0.999. The effect of gravitational acceleration and deceleration is taken into account in the calculation.

---

Fig. 2 Angular distribution of UCNs with \( v = 5 \text{m/s} \). The reflectivity of the UCN container wall

Fig. 3 Angular distribution of UCN of \( v = 1 \text{m/s} \) and \( 3 \text{m/s} \).
A non-isotropic angular distribution appears after traveling in the long tube. The cases of 1 and 3m/s UCN are shown in Fig. 3. The non-isotropic angular distribution appears in all cases, and the angular distribution, itself, depends on the UCN velocity. The UCN density must be deduced while taking into account the effect of $f(\theta, \nu)$. This may explain the unresolved reduction factor of 100 in order of magnitude discussed in Ref. [3].

We propose to place a rotatable UCN mirror in the UCN container above the gravity acceleration tube, as shown in Fig. 4 in order to study the angular distribution of the UCN momentum by measuring the counting rate of UCNs at various rotating angles of the mirror. The designed mirror is a 0.3mm-thick silicon plate coated by nickel; its size is 24mm × 30mm. The rotatable mirror can be moved upward and downward.

![Image of rotatable mirror](image)

**Fig. 4 Rotatable mirror.**

We calculated the effect of the rotatable mirror. The dependence of UCN counting rate on the rotation angle of the mirror ($\eta$) can be expressed as

$$N(\eta) = n \int_0^{\nu_{\text{max}}} dv \int d\Omega f(\theta, \nu) v h(\theta, \eta),$$

(4)

where $h(\theta, \eta)$ is the extraction rate of UCNs with $v = 1[cm/s]$ and $n = 1[cm^{-3}]$ with the rotatable mirror set at $\eta$. The calculated value of $h(\theta, \eta)$ is shown in Fig. 5. The effect of the gravitational acceleration and deceleration of UCN inside the UCN tube was neglected in this calculation, since the difference in the gravitational energy at the top and bottom of the UCN container is ±3% of a kinetic energy of 5m/s for the UCNs.
The dependence of the UCN counting rate on the mirror angle ($\eta$) is proportional to $f \, d\Omega h(\theta, \eta)$ for an isotropic angular distribution(Fig. 6). The UCN counting rate varies by $\pm 1.4\%$ as a function of $\eta$. It is natural to assume that the $f(\theta, v)$ is larger at small $\theta$ than at larger $\theta$ because the UCN counting rate obtained in the experiment is much smaller than the expected counting rate. In this case, the UCN counting rate should be strongly dependent on $\eta$.

In this calculation, the mirror appears suddenly just after the UCN is stored in the UCN tube. Under actual operation, it takes a few seconds to move the mirror at a certain position. This should be corrected in an analysis of the experimental results.

Measurements of UCN counting rate with the rotating mirror may not be sufficient to determine the UCN density, since the velocity dependence of $f(\theta, v)$ is not measured. We are developing a UCN spectrometer in order to measure the energy distribution of UCNs in superfluid $^4\text{He}$. The UCN spectrometer is a UCN detector array covered by material layers. The UCN energy is selected by the UCN reflection on the material layers which have various values of effective potential. A $^6\text{Li}$-drift solid-state detector is a promising candidate.
SUMMARY

In superthermal UCN production at JAERI in 1991, the UCN density in the superfluid \(^4\)He was not determined. We carried out a numerical simulation to study the relation between the UCN density and the counting rate of UCN at the bottom of the gravity acceleration tube. The determination of UCN density without measuring the angular and energy distributions is almost impossible due to the strong dependence of the UCN counting rate on the angular and energy distributions. Measurements of the angular and energy distributions are in preparation. The roughness and reflectivity of the inner surface of the UCN container must be taken into account in order to deduce the UCN density, which is neglected in this simulation. Furthermore, information concerning angular and energy distributions is necessary in order to optimize the geometry of the UCN container and the extraction method of UCNs.

ACKNOWLEDGEMENTS

We gratefully acknowledge Profs. H. Sugawara, H. Hirabayashi, A. Masaike and H. Yoshiki for their kind help in continuing this work. We also thank Dr. T. Ebisawa for his useful suggestions.

References

THE SPECULAR REFLECTION FROM MULTILAYER MIRRORS TO CONSTRUCT THE INTERFEROMETER FOR VERY COLD NEUTRON

Haruhiko FUNAHASHI, Kazuya AIZAWA, Toru EBISAWA, Mitsuhiro HASHIMOTO, Yoshié OTAKE, Toshio TAKAHASHI, Seiji TASAKI, and Hiroshi TOMIMITSU

Dept. of Phys., Kyoto Univ., Kyoto 606-01, Japan
$ Physics Division JAERI, Tokai-mura, Ibaraki, 319-11, Japan
# Kyoto Univ. Research Reactor Institute, Kumatori, Osaka, 590-04, Japan
% Institute for Solid State Physics, University of Tokyo, 106, Japan
* on leave from Ibaraki National College of Technology, Katsuta, Ibaraki, 312, Japan

Abstract

The project of the multilayer mirror interferometer for very cold neutron (MINE) has been in progress for these years in KUR and now also in JRR-3M. The large lattice period ("d" > 50 Å) of multilayer mirrors enable us to construct the neutron interferometer for long wave length with large beam separation. We report about the latest results of the characteristics of the mirrors by the double crystal diffractometer methods.

Introduction

Several attempts have been made to develop neutron interferometry for cold neutron. Ioffe et al. have successfully tested a diffraction-grating neutron interferometer for thermal neutrons[1], and Gruber et al [2] have developed a phase-grating interferometer for very cold neutrons, λ ≈ 100 Å. Now we design MINE (Multilayer Interferometer for cold Neutron) for λ ≈ 10 Å in KUR and also in JRR-3M.

Multilayer Mirror Interferometer

The advantages and applications of "MINE"

We have developed multilayer neutron mirrors using conventional Bragg reflection[3] as shown in Fig.1. Multilayer mirrors are fabricated by deposition two kinds of material with difference refractive indices alternately on a very flat silicon substrate. The reflectivities of multilayer mirrors can be controlled by adjusting the number of layers. The period d of a multilayer mirror is available in the range from about 50 Å to 500 Å, which gives the Bragg condition in terms of 2d by the equation λ = 2d sin θ. The period of a multilayer mirror differs from that of perfect crystal silicon as well as that of grating. Thus, multilayer
mirrors enable us to construct Mach-Zehnder type neutron interferometers with wide beam separation for very cold neutrons as shown in Fig.2. Using magnetic multilayer mirrors, we can control not only polarized neutrons directly by mirrors of the interferometers but also the existence (or non-existence) of the mirror according to the external magnetic field. These advantages of multilayer neutron mirrors would allow us many kinds of applications of interferometry to the phenomena of fundamental physics.
There are some proposed experiments for MINE[4], one is the Michelson type interferometer for very cold neutron to measure the longitudinal coherence length of the cold neutron directly. The experiments using the advantages for the magnetic mirrors are listed here, (1) the delayed choice type experiment, (2) the double-Stern Gerlach type experiment and (3) the search for the neutron-spin-dependent-gravitational interaction, the later two experiments are shown in Fig.3 and Fig.4 respectively. The double Stern-Gerlach type experiment is originally proposed by S.Machida and M.Namiki [5] to test some measurement theories such as the Many-Hilbert-Spaces-Theory [6], the environment theory of Zurek [7] and the Many-World-Interpretation of Everett [8].

![Fig3. the Double Stern-Gerlach Experiment](image)

\[ A_s = \frac{O_s - O_s'}{O_s + O_s'} = \cos(\omega \cdot \theta \pm \phi_{spin}) \]

![Fig4. the Search for Spin Dependence of Gravity](image)
Accuracy requirements

In the interference experiment the relative phase difference between two wave functions in the interferometer must be controlled very accurately to get interference fringe. The schematic view of four important elements to constructs MINE is shown in Fig.5. Here we only discuss the accuracy requirements for the multilayer mirrors and the alignment system, however we are also developing the position sensitive detector.

Fig.5 Elements of Interferometer Experiment

The accuracy requirements for the angle (Δθ) and the position (Δa) of the mirrors should be less than 10^-4 rad → 100 Å / cm, and Δa/λ, which is 100 Å for λ = 10 Å and d = 200 Å respectively. We don’t discuss in details here[9]. A uniform deviation of mirror surface could be compensated by a phase shifter or by adjusting the position of the mirror. On the other hand, vibration and roughness of the mirror surface not only reduce the contrast of the interference pattern, but there is no external means to compensate the reduction effect.

Mirror Characteristics

The roughness of the mirror surface not only from the microscopic point of view but from the macroscopic point of view causes such reduction effects of the contrast as mentioned above. Multilayer mirrors for the interferometer need a high perfection of an one-dimensional lattice. We have precisely measured angular distributions of the specular
reflection (Bragg diffraction) from our multilayer mirrors by the double crystal diffractometer, PNO (λ = 2.0Å) Fig. 6 and ULS (λ = 4.7Å) Fig. 7. The preliminary results of them are shown in the table below.

<table>
<thead>
<tr>
<th>wave length</th>
<th>mirror</th>
<th>R.M.S.of peak (sec of arc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7Å (ULS)</td>
<td>no mirror</td>
<td>2.65 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>mirror1</td>
<td>2.92 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>mirror2</td>
<td>2.76 ± 0.14</td>
</tr>
<tr>
<td>2.0Å (PNO)</td>
<td>no mirror</td>
<td>0.83 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>mirror1</td>
<td>1.30 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>mirror2</td>
<td>0.82 ± 0.04</td>
</tr>
</tbody>
</table>

Fig. 6 Double Crystal Diffractometer "PNO" at JRR-3M; 3G

Fig. 7 Double Crystal Diffractometer "ULS" at JRR-3M; C1-3
Conclusion

We are preparing three kinds of mirrors: Ni-Ti with a layer thickness of 50Å, Ge-Ti with 100Å and Si-V with 200Å, since the accuracy requirements for the position and also the perfection of the surface of the mirrors explicitly depend on the lattice period 2d. Adjustment of mirror position by the piezo actuator system allows us to change the two optical path length, these features of the device would permit us many kinds of applications of the interferometry to fundamental physical phenomena.

Acknowledgement

This work has been performed by using facilities of the Research Reactor Institute, Kyoto University, and the Japan Atomic Energy Research Institute. This work was financially supported by the Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture in Japan; Grant-in-Aid for General Scientific Research (Project number 036403449), Grant-in-Aid for Scientific Research on Priority Areas (Project number 04244103), and Grant-in-Aid for Encouragement of Young Scientists; (Project number 03855066 and 04855060) partly.

References


UCN-VCN FACILITY AND EXPERIMENTS
IN KYOTO UNIVERSITY REACTOR

Yuji KAWABATA, Kiyoshi OKUMURA and Masahiko UTSURO

Research Reactor Institute, Kyoto University,
Kumatori-cho, Sennan-gun, Osaka 590-04, Japan

ABSTRACT

An ultracold and very cold neutron facility was installed in Kyoto University Reactor (KUR). The facility consists of a very cold neutron (VCN) guide tube, a VCN bender, a supermirror neutron turbine and experimental equipments with ultracold neutrons (UCN). The properties of each equipments are presented. UCN is generated by a supermirror neutron turbine combined with the cold neutron source operated with liquid deuterium, and the UCN output spectrum was measured by the time-of-flight method. A gravity analyzer for high resolution spectroscopy and a neutron bottle for decay experiments are now developing as the UCN research in KUR.

INTRODUCTION

The ultracold neutrons (UCN) research started in only two decades ago, and several new research fields have been opened up by using UCN. In the early stage of the study, UCN were directly extracted from the reactor core. However, it is very difficult to extract very low energy neutrons without a significant loss of the intensity, because the neutron
energy is very close to the Fermi pseudo-potential of the barrier materials and the absorption cross-section for UCN becomes very large according to $1/v$ law.

In Gatchina, a vertical guide tube is used to extract neutrons with a somewhat larger velocity at $\text{H}_2$-CNS which is placed in the center of the reactor core. The deceleration of neutrons by the gravity changes them to UCN at the exit of the guide tube.\textsuperscript{25} In Grenoble, a vertical VCN guide tube from the $\text{D}_2$-CNS connected to a neutron turbine advantages of extracting neutrons with a little larger velocity.\textsuperscript{43} A propose of superthermal source has also been also studied in Grenoble\textsuperscript{25} and in Tokai.\textsuperscript{63}

The high intensity UCN sources have opened the possibility of the applications in both fundamental and condensed matter physics, for instance, the electric dipole moment (EDM) of a neutron\textsuperscript{7, 42}, the neutron lifetime\textsuperscript{29}, the gravity spectrometer\textsuperscript{103}, the diffractometer\textsuperscript{111}. Preliminary neutron microscope systems were also constructed and images with some magnifications were obtained.\textsuperscript{12, 133}

In Kumatori, a preliminary UCN generation system has been installed about 10 years ago in Kyoto Univ. Reactor (KUR) which is a 5MW pool type reactor. UCN was generated by a preliminary VCN guide tube and a supermirror neutron turbine.\textsuperscript{142} Recently, a $\text{D}_2$-CNS was installed in a graphite thermal column.\textsuperscript{133} The performance of the UCN generation system was much improved and UCN experiments are in progress.

**VCN EQUIPMENTS IN KUR**

The general layout of the VCN-UCN facility in KUR is shown in Fig. 1. It needs special techniques to extract VCN because it has very low energy and a wide beam divergence in the VCN guide tube.

A VCN guide tube in horizontal arrangement\textsuperscript{149} was inserted deeply into the graphite thermal column close to the cold neutron source (CNS). The cold moderator of CNS is liquid deuterium. The in-pile-portion of the VCN guide tube is specially made to withstand the nuclear irradiation and
Fig. 1 General layout of the VCN-UCN facility in KUR

Neutron Spectrum from VCN-GT (center : CNS=ON)

Fig. 2 Neutron spectrum at the center of the VCN guide tube exit with the CNS operation

heating. The characteristic wavelength of the VCN guide tube is 23.5Å. The neutron spectrum measured by the time-of-flight method is shown in Fig. 2.

After the horizontal VCN guide, the VCN beam is curved upward sharply by a VCN bender in order to fit to the supermirror neutron turbine which converts VCN to UCN. The neutron beam in the bender is
divided into 5 sub-sections by nickel evaporated silicon wafer mirrors. The radius of curvature is 5.24m and the characteristic wavelength is 48Å. The neutron flux distribution measured by the neutron radiography film shown in Fig.3 indicates the characteristic distribution of a curved guide superposed by the fine structures due to sub-sections.

Fig.3 Neutron flux distribution of the VCN bender exit measured by the neutron radiography film. The optical density is proportional to the neutron flux.

UCN PRODUCTION BY NEUTRON TURBINE UNDER CNS OPERATION

The supermirror neutron turbine is a mechanical type UCN source using neutron reflections on moving mirrors.\cite{17} Figure 4 shows a diagram of the supermirror neutron turbine with a set-up of the time-of-flight spectrum measurement. Each set of blade on the wheel is made of 3 flat supermirrors. The diameter of the wheel is 1m and the velocity of the blade is about 25m/s. The incident VCN with the velocity of about 50m/s are reflected and decelerated to about 5m/s.

The neutron turbine in the reported study of the transmission experiments generated UCN pulsed beam in order to make a time-of-flight

Fig.4 Structure of the supermirror neutron turbine for UCN transmission experiments measurement. (Now it provides a continuous UCN output with the blades covering whole the wheel.) UCN output from the blade is conducted to a 4He UCN detector by a short nickel UCN guide tube with the length of 150mm, and thus the total axial neutron flight path of UCN is 190mm. The axial velocity is defined here the velocity component parallel to the axis of the UCN guide tube. The measured UCN transmission through a 50 μm thick nickel foil is shown and compared with calculations in Fig.5.

Fig.5 UCN transmission through the 50 μm thick nickel foil. Neutron absorption effect by nickel increases according to the 1/v law. The axial neutron velocity is v in vacuum and it changes to v' in nickel by the refraction effect.
Although a nickel thin foil is sometimes used as a filter to remove UCN, the figure shows the absorption factor cannot be neglected. Thickness of nickel filter should be about 2000Å to have a sharp step of the transmission at the critical velocity as a good filter. The measured transmission shows the slight deviation from the 1/v law. The reason is expected to be the diffraction effects from the magnetic domain structure of the nickel foil.

Figure 6 shows the UCN output depending on the rotational speed of the turbine blade. The incident velocity of the neutron to be decelerated to UCN is about twice as fast as the velocity of the blade. Thus, the UCN output depends on the incident neutron flux at the corresponding energy region at the turbine speed as well as the neutron reflectivity of the supermirror blades. Faster neutrons have higher neutron flux in general, while lower reflectivity on the supermirror blades. This is the mechanism of the broad peak of the UCN intensity without the CNS operation in Fig.6. When the CNS is operated, the neutrons coming out from the deuterium moderator should penetrate through the aluminum walls. Absorption and scattering effects at the aluminum wall cause more loss for slower neutrons. Therefore, the optimum blade speed becomes faster when the CNS is operated. It suggests that the higher UCN flux would become available if the turbine wheel is rotated somewhat faster than shown in Fig.6.
GRAVITY ANALYZER USING UCN

A prototype gravity analyzer for the neutron scattering using UCN has been constructed.\textsuperscript{19,20} It has high resolutions for both energy and momentum transfers. The principle of the energy analysis is "fall-focusing".\textsuperscript{21} The reflection mirrors are arranged whole around the scattering axis in order to gather most of the scattered neutrons effectively except the uppermost and lowermost positions.

Vertical view of the gravity analyzer is shown in Fig.7. The scattering angle is divided into 5 sections to analyze the momentum transfers. The momentum resolution is designed as $2 \times 10^{-3}$ Å\(^{-1}\). At present, the reflection mirrors in the 2nd and 4th regions among of 5 regions are installed. The scattered neutrons with the velocity between 4m/s and 13m/s will be measured because supermirrors with the critical velocity of about 13m/s are deposited on the reflection mirrors and aluminum walled detectors are used. The energy resolution is expected to be about 30neV from the numerical analysis.

The phenomena of UCN scattering to be studied by using the present
analyzer would be different from those observed with other type of higher resolution spectrometers using thermal or cold neutrons in case of inhomogeneous samples such as particles suspended in liquid. The effect of neutron refraction on the sample particles will be more marked in case of UCN. In such cases, the UCN spectrometry may become effective approach for the studies of possible microscopic surface dynamics.

NEUTRON BOTTLE

Neutron bottle experiment for measuring the neutron decay $\beta$-energy is under preparation as a collaboration with the members of Tohoku University and INS, University of Tokyo. The advantage of the supermirror as the wall of the bottle in order to contain more neutrons was pointed out after numerical simulations. The $\beta$-ray detectors with the nickel evaporated surface to reflect UCN are prepared and showed satisfactory performances for the $\beta$-spectroscopy.

Preliminary experiments with a test bottle made of several kinds of wall materials are now carried out in the vacuum chamber of the neutron turbine.

CONCLUDING REMARKS

The UCN-VCN facility was installed in KUR and UCN is generated under CNS operation. The gravity analyzer and the neutron bottle experiments are in progress. The UCN flux in our facility at KUR is suitable for developing several new types of novel equipments described here, since the machine-time is enough and the facility has a good flexibility for these experiments.

REFERENCES

NEUTRON OPTICS USING TRANSVERSE FIELD
NEUTRON SPIN ECHO METHOD

Norio ACHIWA, Masahiro HINO, Seiji TASAKI*, Tsunekazu AKIYOSHI*,
Toru EBISAWA*, Yoshihiro YAMAUCHI, Hiroyuki TAKAKURA
Department of Physics, Kyushu University 33, Higashi-ku, Fukuoka, 812 Japan
*Research Reactor Institute, Kyoto University, Kematori-cho, Osaka-ku, 590-04 Japan

Abstract

A neutron spin echo (NSE) spectrometer with perpendicular magnetic field
to the neutron scattering plane, using an iron yoke type electromagnet has been
developed. A combination of cold neutron guider, supermirror neutron polarizer
do double reflection type and supermirror neutron analyzer was adopted for the
spectrometer. The first application of the NSE spectrometer to neutron optics
by passing Larmor precessing neutrons through gas, solid and liquid materials
of several different lengths which are inserted in one of the precession field have
been examined. Preliminary NSE spectra of this sample geometry are discussed.

1 INTRODUCTION

The main features of conventional neutron spin echo (NSE) spectroscopy1) in
quasi-elastic neutron scattering when the sample is located between the two spin
precession fields of neutrons: (i) Energy resolution and monochromation are in principle
decoupled, resulting in good neutron economy. (ii) Direct information of NSE signal is
S(q, ω), Fourier integral of usual scattering law S(q, ω).
Neutron spin echo appears when the numbers of the Larmor precession, N_0 and N_1,
before and after the π spin flipper are equal. The number the Larmor precession can
be scanned by the field scanning of the second precession field. The change of neutron
speed before and after a sample is proportional to the shift of the echo field. The
generalised resultant change in the numbers of the Larmor precessions before and after
the scattering for non-identical field integrals is:

\[ \delta N = N_0 - N_1 = \frac{\gamma L}{2\pi} \left[ \frac{l_0 H_0}{V_0} - \frac{l_1 H_1}{V_1} \right] \]  \hspace{1cm} (1)

where \( \gamma_L = 2.916 \text{ kHz/Oe} \) is the Larmor precession constant for neutrons \( l \) and \( H \) refer
to the field lengths and fields, \( V \) is the neutron velocity, and the subscript 0 and 1 refer
to the situation before and after the scattering.

Now, we consider new spinecho geometry, when a sample is inserted in one of the
neutron precession fields. This geometry is just the same as neutron spin interferometry
proposed by Baryshevskii2). Neutrons passing through a refracting material would
change their speed proportional to the refractive index of neutrons. Then, the number of Larmor precessing neutrons passing through material changes and the change of neutron speed can be detected as a shift of the echo point. A refractive index of neutrons through material is characterized by the optical potential $V = (2\pi\hbar^2/m)N_p b$, where $N_p$ is nuclear density and $b$ is coherent length. Then,

$$n^2 = 1 - \frac{V}{E} \pm \frac{\mu B}{E}$$  \hspace{1cm} (2)$$

where $E$ and $\mu$ are kinetic energy and magnetic moment of neutron, respectively; the minus sign corresponds to the spin orientation along the field $B$. Since $(n - 1)$ is proportional to $\lambda^2$, longer the wavelength easier to detect the effects of refractive index.

It would not be so simple, when we consider forward scattering by polycrystal or liquid. Multiple scattering process in polycrystal would change path length of neutrons for forward scattering even if wavelength is longer than the Bragg cut off wavelength of the material. NSE phase is very sensitive to the change of neutron path. In case of liquid, forward scattered neutrons would exchange energy with density fluctuation mode in liquid even if $q=0$. So the NSE spectra through gas, single crystal, polycrystal or liquid in one of the precession field would have variety. We have examined such cases.

A combination of cold neutron guide tube, supermirror neutron polariser of double reflection type and supermirror neutron analyser whose devices have been developed by us$^3$ is very effective for NSE spectroscopy of long wavelength. Moreover, NSE spectrometer with vertical magnetic field using iron yoke has following characteristics; very low stray magnetic field outside of the electromagnet, wide angle covering of scattered neutron detection, and the perpendicular condition between neutron scattering vector and the magnetic field at the sample position.

2 TRANSVERSE FIELD NSE-SPECTROMETER

The schematic lay-out of the KUR-NSE spectrometer at the CN2 cold neutron guide tube in the Kyoto University Reactor (5MW) is shown in Fig. 1. The supermirror neutron polariser of double reflection type of which pairs are assembled in a Soller type, can provide collimated monochromatic polarised beam with $\delta\lambda/\lambda \sim 10\%$ and without $\lambda/2$ component. Magnetic supermirrors are made of FeCo-Ti or FeCo-V multilayers with varying spacings from 70 Å to 90 Å. The wavelength of neutrons can be varied by changing the scattering angle of monochromator and the angle of double reflection from 4 Å to 10 Å with wavelength resolution of 10%. Vertical magnetic fields are provided by electromagnets with iron-core, all of which have the same cross-sectional figure shown in Fig. 2.
Fig. 1. Layout of the transverse field NSE spectrometer. In the present experiments a sample is inserted in one of the precession field.

Fig. 2. Cross-sectional view of electromagnet with extra-pole pieces improving the field homogeneity.

The inhomogeneity of relative field integral, $\delta D/D$ along the paths of neutrons is an important factor in determining the maximum field $H_{max}$ utilisable in a spin echo instrument. In order to reduce the field integral inhomogeneity lower than $10^{-4}$, the field distribution along vertical direction in the magnet is improved by adding extra-pole piece so as the maximum field strength to occur at the middle height of magnetic gaps.

In order to adjust the magnetic field of the two $\pi/2$ neutron spin turners and $\pi$ spin turner coils of Rekveld-type (three dimensional arbitrary field adjustable coil), all currents of three directional coils were digitally scanned automatically.

The KUR-NSE machine arms of the first precession magnet and the second precession magnet can rotate freely around the polariser table and the sample table automatically. Summary of designed parameters of KUR-NSE spectrometer are listed in Table 1.

The energy resolution of NSE spectrometer is determined by the maximum observable NSE field integral. The maximum observable NSE field is depend on not only the inhomogeneity of the field integral but also the resolution of monochromatic neutron beam. So it is necessary to simulate the NSE patterns for the given conditions. The simulation has been carried out following the Komura's matrix analysis\(^4\). In table 1, the resolution parameters of the KUR-NSE are given.
Table 1. Summary of the resolution parameters of the KUR-NSE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic field integral</td>
<td>D 0.12 Tm</td>
</tr>
<tr>
<td>incident wavelength of neutron</td>
<td>λ 5.7 Å</td>
</tr>
<tr>
<td>turn number of Larmor precession</td>
<td>N 5043</td>
</tr>
<tr>
<td>Fourier time</td>
<td>t 4.14 nsec</td>
</tr>
<tr>
<td>spectral resolution</td>
<td>ΔE=ℏ/t 159 neV</td>
</tr>
<tr>
<td>energy resolution</td>
<td>δE=2δD·E/D 1 μeV</td>
</tr>
</tbody>
</table>

3 EXPERIMENTAL RESULTS AND DISCUSSIONS

First of all we have examined forward scattering through 90 cm of hydrogen gas set in one of the precession magnet. Figure 3(a) shows comparison of NSE signals observed through hydrogen gas and air, when turn numbers of Larmor precession \( N_1=1681 \). The incoherent scattering of the hydrogen gas scattered about 30% of incident neutrons but the pattern of NSE signal through air agreed well with that of the hydrogen gas, which is multiplied by a factor 1.32. Similar experiment was carried out through 40 cm long Si single crystal in one of the precession magnet for the number of Larmor precessions \( N_{40cm}=840 \). Though the transmission probability of neutron through the Si crystal is 42%, the NSE signal without sample is well reproduced by the normalized signal through the Si crystal. The NSE signal through Be polycrystal of 16 cm long with and without sample are compared in Fig. 4(a) and (b) for \( N_{80cm}=840 \). The agreement of normalised signals between with and without sample is rather well except small width change of the envelope and polarization though the transmission probability is 20%. The variation of polarization and width of the envelope of NSE signals against thickness of Be metal are plotted in Fig 4(c) and (d).

![Spin echo H₂ and Air(1681 turns)](image1)

![Spin echo Si and Air(840 turns)](image2)

Fig. 3. a) NSE signals through air and H₂ gas of 80 cm long are compared, for turn number of Larmor precessions, \( N_{80cm}=1681 \) and neutron wavelength \( λ=5.7 \) Å.  

b) NSE signals through air and a Si single crystal of 40 cm long set in one of the precession magnet for \( N_{40cm}=840 \) and \( λ=5.7 \) Å.
Fig. 4. a) NSE signals through air and b) Be polycrystal of 16 cm long for turn number of Larmor precessions, N1=871 and neutron wavelength λ=5.7 Å. c) Variation of envelope width of NSE signals against thickness of Be polycrystals, d) variation of polarization of NSE signals against thickness of Be polycrystals for N1=871 and λ=5.7 Å.

Fig. 5. a) NSE signal for N1=871 without sample and b) NSE signal through D2O liquid of 2.5 cm.

On the other hand, transmitted NSE signal through liquid D2O of 25 mm long showed remarkable change of pattern in NSE signal for the transmission probability of 20% which is the same value of 16 cm Be polycrystal, as shown in Fig. 5 b). We can find apparent difference in the NSE signals through the polycrystal and liquid. NSE
signal through 5cm long of liquid D₂O showed a completely destroyed echo pattern. For q=0 limit, the scattering in liquid correspond to density fluctuation and the NSE signal would give information of quasielastic scattering function S(0,t). It is important to try the q=0 NSE experiment for liquid metal because light scattering can not be used.

Refractive indices for Si and Be metals are 2×10⁻⁵ and 5×10⁻⁵, respectively for λ=5.7 Å. The stability of precession field for a week was worse than 1×10⁻⁵ so the presice refractive index could not be determined in this experiment. But we have observed an effect of multiple scattering for Be polycrystal with increasing thickness of the sample. And for liquid D₂O NSE signal showed apparent decrease of polarization due to a quasielastic scattering at q=0 with increasing sample thickness.

4 References

1) F. Mezei, 'Neutron Spin Echo', (1979) Springer-Verlag, Lecture Notes in Physics, 128.


Research on Highly Excited States of Nucleus
by Slow Neutrons

Makio OHKUBO
Department of Physics, Tokai Establishment
Japan Atomic Energy Research Institute

ABSTRACT

To investigate highly excited states of compound nucleus, neutron transmission measurements were made on the resonances of Sb-121 and Sb-123 using a time-of-flight spectrometer at the JAERI electron linac. Resonance of about 400 levels below 5.3 keV are analysed, and average level spacings, s-wave strength functions are deduced. As a model of highly excited states, a recurrence model is developed, where effective number of degrees of freedom and the nuclear temperatures of the compound nuclei are derived.

1. INTRODUCTION

Crystalline structures of materials are analyzed by the diffraction of thermal or cold neutrons, where the neutron wave lengths are comparable to the lattice sizes concerned. Using neutrons of more shorter wave length, information on highly excited states of nucleus is extracted. A compound nucleus formed by slow neutron resonance reaction is thought to be chaotic, and it is interesting to discuss a model of the neutron resonance reactions. Neutron cross sections are observed mostly by the neutron time-of-flight experiments using pulsed accelerator neutron source. The observed cross sections and the resonance parameters are compiled in a reference Data Book [1,2] for almost all the nuclides. These data are important for the nuclear reactor technology, as well as basic data for neutron-nucleus interaction.

In this article, are briefly described neutron transmission measurements on Sb-121 and Sb-123 in the resonance region, using TOF spectrometer of JAERI electron linac. Resonance energies and neutron widths are deduced on many resonances below 5.3 keV. Average level spacings and s-wave neutron strength functions are also deduced. We have considered a model of highly excited chaotic states, which recurrs approximately with a period h/D. By the model, effective number of degrees of freedom play roles in the compound nucleus are deduced. These numbers are compared to the exciton numbers of Fermi-gas. Nuclear temperatures are also derived from the
recurrence model. Time structures and energy spectrum of resonances are deduced by the recurrence model.

2. Total Cross Section Measurements

The lowest resonance of antimony at 6.2 eV is often used for the energy calibration of reactor neutron beam. Resonance parameters of natural antimony up to 3 keV were reported by Wynchank et al. [3], and on separated isotopes by Muradyan et al. [4]; Sb-121 up to 2.5 keV, and Sb-123 up to 4.1 keV. There are some discrepancy between the data.

In order to get accurate resonance parameters in wide energy region, transmission measurements on Sb-121 and -123 were carried out at a 47-m TOF station of the JAERI electron linac [5]. Neutrons were produced at a water cooled tantalum target bombarded by the electron beam from the linac, of which energy was 120 MeV, peak current ~ 3A, pulse width 25ns and repetition rate max. 600 pps. The neutrons were moderated by a surrounding moderator to have white spectrum, and were traversed to the TOF station through an evacuated flight tube. In the station, as shown in Fig. 1, a 6Li-glass neutron flux monitor, a transmission sample, and a 6Li-glass main detector (38mm x 12.7mm, NE912) was placed. A boron filter was used to cut off slow neutrons.

![Fig. 1](image)

**47-m Time of Flight Station**

Thicknesses of antimony samples were 2, 5, 10 and 35 mm for Sb-natural, 2 and 10 mm for Sb-121 for Sb-123, respectively. The separated isotope samples of metallic powder were rent from the Oak Ridge National Laboratory Isotope Pool.

The neutron pulses of the main detector were accumulated in a 4096 channel time analyzer with the minimum channel width 31.25ns. The data processing and resonance analyses were made by a large computer FACOM-M380 at the JAERI computing center. After subtraction of backgrounds, neutron transmissions for these samples were deduced from the ratio of the sample-in spectra to the open-beam spectrum with the normalization of neutron fluence. The backgrounds were estimated from the counts at the black resonances of cobalt (132eV), manganese (337eV), and aluminum (35 keV). Energy scale of the TOF system was calibrated using the aluminum resonances at 5.9035 and 119.75 keV. The accuracy of the neutron flight path length was
less than $1 \times 10^{-4}$. The raw data of the neutron time of flight spectra for the open beam (without any sample), and transmissions for the Sb-121 are shown in Fig. 2, where the energy region is from 5 eV to 170 eV and the sample thickness was 10 mm.

**Fig. 2**

The resonance parameters (resonance energies and reduced neutron widths $\Gamma_0$, and total width $\Gamma = \Gamma_n + \Gamma_r$ where radiation width $\Gamma_r$ are assumed to be 100 meV) were deduced by fitting the Breit-Wigner formula to the transmission data, using a modified single level Atta-Harvey area analysis program. Assuming all the levels are s-wave levels, the reduced neutron widths were determined for 188 levels of Sb-121, and for 202 levels of Sb-123 up to 5.3 keV. The resonance parameters of Sb-121 from 2.5 keV to 5.3 keV, and of Sb-123 from 4.1 keV to 5.3 keV are newly determined. Cumulative number of levels vs. neutron energy for Sb-121 is shown in Fig. 3a, and for Sb-123 in Fig. 3b, changing cut-off values of $\Gamma_0$ as described in the previous work.[6] From these figures, average level spacings for mixed ensembles of s- and p-wave levels were deduced to be:

- Sb-121: $D = 10.3 \pm 0.5$ eV, $E < 0.6$ keV
- Sb-123: $D = 20 \pm 1$ eV, $E < 1.3$ keV
where the missing levels may be small in these energy regions. Cumulative values of \( g_{fn} \) vs. neutron energy for Sb-121 are shown in Fig. 4a, and for Sb-123 in Fig. 4b. The s-wave strength functions \( S_0 \) were deduced to be

\[
\begin{align*}
\text{Sb-121} & \quad S_0 = (0.24 \pm 0.03) \times 10^{-4} \quad E < 5.3 \text{ keV}, \\
\text{Sb-123} & \quad S_0 = (0.25 \pm 0.03) \times 10^{-4} \quad E < 5.3 \text{ keV}.
\end{align*}
\]

which are nearly the same values. The previously compiled strength functions for these isotopes are somewhat different for the two isotopes; 0.3 ±0.05, and 0.25 ± 0.07, respectively. [1] By the present measurement, it is proved that the difference is due to the local variation of the strength functions. A similar case is found in silver isotopes where the difference in previous values of the strength functions of Ag-107 and Ag-109 is much reduced by new measurements in a wider energy region. [7]

3. Recurrence Model of Compound Nucleus

A compound nucleus formed by slow neutron resonance is at an excitation energy \( E_X = E_k + S_n \), where \( E_k \) is neutron kinetic energy and \( S_n \) is neutron separation energy (5~8 MeV). In the compound nucleus, many degrees of freedom are excited and considered to be chaotic. However, because of sharp energy selectivity and very long life time (\( \sim h/\gamma \)) of the resonances, the resonance states are nearly closed systems. We consider that the phases of system recur repeatedly with a definite time period, as in all the resonance phenomena in classical physics.

We assume that a resonance state is approximated by a set of independent harmonic oscillators, with angular frequencies \( w_1, w_2, \ldots \). Excitation energy \( E_X \) is divided into these oscillators with a following relation.

\[
E_X = \frac{h(w_1 + w_2 + \ldots + w_M)}{(2\pi)} \quad \ldots (1)
\]

For two classical harmonic oscillators, the phase point \((X, Y)\) depicts a straight line, in a square of \((2\pi \times 2\pi)\) periodic boundary, where \( t \) is time and \( X = w_1t \) and \( Y = w_2t \) phase
angles of the two oscillators. If the point start at the origin at t=0, the locus black out the square after infinite time, and does not return to the origin in general. Here we introduce an allowable phase angle region around the origin, and when the point come back into the region, we regard it as the recurrence, as shown in Fig. 5. The recurrence frequency is a function of speed of the

\[ f(2) = \frac{d_2 w_1 + d_1 w_2}{(2\pi)^2} \]  

(2)

where \(d_1, d_2\) are allowable phase angles in radian.

As to the allowable phase angle error \(d\), we postulate that

\[ d = 1 \text{ radian} \]  

(3)

which is narrower than that expected from the uncertainty relation for the quantum system. For \(M\) oscillator system, the recurrence frequency \(f(M)\) can be described as

\[ f(M) = \left(\frac{1}{2\pi}\right)^{M-1} \frac{w_1 + w_2 + \ldots + w_M}{(2\pi)} \]  

(4)

The recurrence time of the compound nucleus is formally given by [8]

\[ \frac{h}{D} \]  

(5)

where \(D\) is average level spacing for the same \(J\pi\) resonances, and \(h\) is the Plank's constant. From the eq.(1), (4) and (5), we get a simple relation as follows.

\[ \frac{E_X}{D} = (2\pi)^{M-1} \]  

(6)

or \[ M = 1 + \frac{\ln(E_X/D)}{\ln(2\pi)} \]  

(6A)

From the eq.(6), effective number of independent oscillators \(M\) which play role in the compound nucleus are derived exactly using \(E_X\) and \(D\) observed by the neutron experiments.[1] For
example in U-238 resonances, $E_x = 4.806$ MeV, $D=17.7$ eV, and $M$ values is calculated to be $M=7.81$. $M$ values versus target mass number are shown in Fig.6. For Sb-121 and Sb-123, $E_x=6.806$, and 6.469 MeV, $D=18$, and 38 eV for same spin states, respectively, and $M$ are deduced to be 7.99 and 7.55, respectively.

![Graph showing $M$ values and $n_{ex}$ vs. mass number.](image)

Fig.6 M values and $n_{ex}$ vs. mass number.

Trend of $M$ vs. mass number is clear, as follows:
1) $M$ ranges from 2 for light nuclei to 10 for heavy nuclei.
2) For neutron magic nuclei $N=28$, 50, 82, and 128, $M$ values decrease rapidly to make dips.
3) For $A > 100$, $M$ values for odd nuclei are about 1.5 larger than that for the neighbouring even-even nuclei systematically.
4) For even-even isotopes in deformed region ($A = 150-180$), $M$ values decrease about 1 for the increase of 4 neutrons.

$M$-values calculated here are compared with the exciton numbers by the Exciton Model of the compound nucleus. In the exciton model of Fermi gas, the number of excitons $n_{ex}$ is roughly given by[9]

$$n_{ex} \approx \left( \frac{g_0 E_x}{2} \right)^{1/2}$$

(7)

where $g_0$ is the single particle level density at Fermi energy for nucleus of mass $A$ which is approximately given by $g_0 = A/13$ (1/MeV) In Fig.6, $n_{ex}$ is shown as curves for $E_x = 2$ to 10 MeV. It is stressed that the $M$ values calculated by the recurrence model are in well agreement with $n_{ex}$, though the nuclear model they based on are of very different nature.

4. NUCLEAR TEMPERATURE

Nuclear temperature $T$ is derived assuming that the $M$ values is proportional to $E_x$.

$$T = \left( \frac{1}{\frac{2E_x}{D}} \right)^{-1} = \frac{E_x}{M \ln(2\pi) - 1}$$

(8)
For many nuclei $T$ are derived from $E_X$ and $M$, and are shown in Fig. 7. For even-odd target nuclei, $T$ are systematically higher than that of even-even and odd-even nuclei in the same mass region. No correction is made on $E_X$ and $D$ to calculate $T$ by the eq. (8). For Sb-121 and -123, $T$ are deduced to be 0.50 MeV for both isotopes. It is stressed that the temperature derived by eq. (8) are in good agreement with those given by Gilbert and Cameron (G-C)[10], especially for medium and heavy nuclei. For the light nuclei A<60 and Pb-isotopes, the agreement becomes poor.

The agreement of the nuclear temperatures derived here and that of G-C suggest the reasonability of the recurrence model, though the two nuclear models are of very different nature.

5. Time Structures

We propose a recurrence model of neutron resonance reactions, described below. On a target nucleus the incident neutron wave is divided into two components. The first component passes by the target nucleus, and the second one coalesces on the nuclear surface and quickly penetrates into the nucleus with an absorption time of $10^{-21}$s. We call the initial phase as "coalescent phase", where it correspond to the instance of concentration of neutron density on the surface of the compound nucleus. The penetrating component excites many modes of neutron density oscillations in the compound nucleus, as described above, and the phase of these oscillations recur to the initial one with a definite time period repeatedly, during life time of the resonance. Interference between the two components take place when the penetrating component build up on the nuclear surface(coalescent phase). There are many possible ensemble of oscillators in the compound nucleus, composed of oscillators with frequencies $(w_1, w_2, \ldots, w_M)$. Among these, only one mode is selected by the interference with passing by component which have definite period. The phase coherency is kept during level life time $\lambda$, and decay is due to
(n,n) and (n,γ) reactions. In Fig. 8, intuitive description of the coalescent phase, the construction of neutron density wave on the compound nuclear surface, and the lifetime envelope are shown. By the Fourier transform of the pulse array, energy spectrum can be obtained as shown in Fig. 9. The first component is envelope function (strength function of giant resonance nature) and the 2nd term is equidistant fine structure resonances with a spacing D, with a width $\Gamma$. Three fold uncertainty relation are derived; $W \sim h/P$, $D \sim h/\tau$, $\Gamma \sim h/\lambda$, where $W$: single particle width and $P$: partitl time.

![Fig. 8 Time structure of neutron density on the compound nucleus.](image1)

![Fig. 9 Energy Spectrum](image2)

**References**

8) J. M. Blatt and V. F. Weisskopf: Theoretical Nuclear Physics, John Wiley and Sons (1952) p387
10) A. Gilbert and A. G. W. Cameron; Canad. J. Phys. 43(1965)1446
PNO-APPARATUS AND ITS TEST USE FOR NEUTRON INTERFEROMETRY

*Hiroshi TOMIMITSU, *Kazuya AIZAWA, *Yuji HASEGAWA and *Seishi KIKUTA

*Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

*Department of Applied Physics
University of Tokyo
Hongo, Bunkyo-ku, Tokyo-to, 113 Japan

ABSTRACT

Special apparatus "PNO" of multiutility in the so-called precise neutron optics, such as double or triple crystal diffractometry, interferometry, etc., including neutron diffraction topography, was settled at 3G beam hole in the JRR-3M. In the symposium, several applications of the PNO apparatus are presented as 1) very small angle neutron scattering tool with double crystal arrangement, 2) the characterization of the quality of artificial multilayer lattices made of Ti-Ni by a triple crystal arrangement, 3) the characterization of Ni-base superalloy single crystals by the diffraction topography, which are presented in individual sessions. Preliminary test of the neutron interferometry was also tried with the PNO apparatus. Usual monolithic Si LLL-type interferometer was used with an AI phase shifter in the neutron beam paths. The periodicity of the measured intensity curve was well corresponded to the expected one. The best contrast of the intensity curve was measured as high as 43%. The utility of the PNO-apparatus for neutron interferometry was, thus, approved.

INTRODUCTION

A special apparatus named "PNO" has been settled at 3G beam hole of JRR-3M in JAERI (Fig. 1), which was designed, making use of the dynamical diffraction phenomena of thermal neutron by perfect crystals, for multi-use in the field of so-called precise neutron optics, such as multi-crystal precise diffractometry, very (ultra)-small angle neutron scattering (VSANS), neutron interferometry (IFM), and neutron diffraction topography (NDT). The PNO has one normal precision goniometer for precise monochromation after the rough one with double PG-crystals, two high precision goniometers for the second- and the third-crystal, one double-axis high precision goniometer with the minimum distance between the axes of 9cm, one specially designed goniometer for topography and three high precision beam narrowers. All elemental equipments mentioned above are completely remote-controlled with a conventional personal computer, on an air-cushioned vibration-free table in a heat-insulated chamber, where the temperature is precisely controlled at the RT± 0.01°C.

In the present symposium, several applications of the PNO apparatus are presented as 1) VSANS-experiment with double crystal arrangement, 2) the characterization of the quality of artificial lattices made of Ti-Ni multi-layers by the triple crystal arrangement, 3) the characterization of Ni-base superalloy single crystals by the NDT-method, which are presented in individual sessions.
The neutron interferometry (IFM) was also tested preliminarily with the PNO apparatus. Usual monolithic Si LLL-type interferometer was used. As the Al-plate set, as the phase shifter, on one of the two neutron beam paths between the splitter and the mirror of the interferometer was rotated step by step, the phase of the neutron beam arriving at the analyzer of the interferometer were changed sinusoidally, accordingly the measured intensity of the neutron beam behind the analyzer was changed sinusoidally. The periodicity of the measured intensity curve was well corresponded to that expected from the scattering radius $b$ of the Al. The utility of the PNO-apparatus for neutron interferometry was, thus, approved.

![Diagram of the PNO-Apparatus](image)

Fig. 1. Bird's Eye View of the PNO-Apparatus at JRR-3M.

**DESIGN AND COMPOSITION OF THE PNO**

The PNO-apparatus was designed after the following principles:

1. the PNO is desirable to be for multi-purposes, so as to carry out many kinds of experiments in the field of precise neutron optics,
2. the PNO should have the highest precision, so as to carry out those experiments with the precision of 0.01 sec. of arc, and
3. stable environment is necessary for the PNO, in order to carry out those precise experiments successfully during rather long period up to 24 hrs.

The PNO is composed of the elemental equipments as shown in Table 1, almost all of which are established in X-ray field and only a little modified for the neutron-use. Every elementary equipments listed in the Table 1 can be connected with one another for requirements, and, in addition, the beam narrowers and the detectors in the noise-shielding can be set on the arms of the precise goniometers, accordingly, the resultant compact set for a special experiment can be fully remote-controlled by a conventional personal computer.
Table 1. Elemental Equipments of the PNO and Their Performance.

<table>
<thead>
<tr>
<th>Equipment (Quantity)</th>
<th>Range of Movement</th>
<th>Mechanical Precision</th>
<th>Min. Unit Control</th>
<th>Min. Read. of Encoder</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'st Goniometer(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Rotation(1)</td>
<td>360°</td>
<td>&lt;0.005°</td>
<td>1°/10000</td>
<td>0.001°</td>
<td>Manual Control</td>
</tr>
<tr>
<td>Tilt Change(2)</td>
<td>±20°</td>
<td>&lt;0.005°</td>
<td>0.8°/1000</td>
<td>None</td>
<td>Manual Control</td>
</tr>
<tr>
<td>Translation(1)</td>
<td>25mm</td>
<td>10μm/50mm</td>
<td>1μm</td>
<td>0.001mm</td>
<td></td>
</tr>
<tr>
<td>Detector Rotation(1)</td>
<td>360°</td>
<td>&lt;0.005°</td>
<td>1°/10000</td>
<td>0.001°</td>
<td></td>
</tr>
<tr>
<td>Precise Goniometer(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Rotation, Coarse</td>
<td>360°</td>
<td>&lt; 10°</td>
<td>15°/100</td>
<td>0.0001°</td>
<td>Exchangeable by Remote-Clutch System</td>
</tr>
<tr>
<td>Fine</td>
<td>±10°</td>
<td>&lt; 10°</td>
<td>1°/200</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Tilt Change(2)</td>
<td>±17°</td>
<td>&lt;0.005°</td>
<td>0.8°/1000</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Translation(1)</td>
<td>25mm</td>
<td>10μm/50mm</td>
<td>1μm</td>
<td>1μm</td>
<td></td>
</tr>
<tr>
<td>Detector Rotation(2)</td>
<td>360°</td>
<td>&lt;0.005°</td>
<td>1°/10000</td>
<td>0.001°</td>
<td></td>
</tr>
<tr>
<td>2-Axis Goniometer(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Rotation(2)</td>
<td>±2.5°</td>
<td>&lt; 5°</td>
<td>1°/200</td>
<td>None</td>
<td>*360° Manual, Minimum Distance=9cm</td>
</tr>
<tr>
<td>Tilt Change(4)</td>
<td>±15°</td>
<td>&lt;0.005°</td>
<td>0.8°/1000</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Goniometer for NDT(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample Rotation(1)</td>
<td>360°</td>
<td>&lt;0.005°</td>
<td>1°/10000</td>
<td>0.001°</td>
<td></td>
</tr>
<tr>
<td>Tilt Change(1)</td>
<td>±17°</td>
<td>&lt;0.005°</td>
<td>0.8°/1000</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Traverse(1)</td>
<td>±25mm</td>
<td>1μm/50mm</td>
<td>1μm</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Detector Rotation(1)</td>
<td>360°</td>
<td>&lt;0.005°</td>
<td>1°/10000</td>
<td>None</td>
<td>Narrover for Incident and Diffracted Beams</td>
</tr>
<tr>
<td>Beam Narrowers(2)</td>
<td>±25mm</td>
<td>50μm/50mm</td>
<td>(0.01mm)</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Beam Narrowers(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horizontal Position(1)</td>
<td>±25mm</td>
<td>2μm/50mm</td>
<td>1μm</td>
<td>1μm</td>
<td>Direct Read</td>
</tr>
<tr>
<td>Vertical Position(1)</td>
<td>±50mm</td>
<td>(0°)</td>
<td>(0.01mm)</td>
<td>None</td>
<td>Manual Control</td>
</tr>
<tr>
<td>Narrowing Blade(4)</td>
<td>0~25mm</td>
<td>50°</td>
<td>(0.01mm)</td>
<td>None</td>
<td>Manual Control</td>
</tr>
</tbody>
</table>

FOR THE STABLE ENVIRONMENT

The PNO is regulated in temperature, vibration and noise by the multiple system as schematically shown in Fig. 2. For the chamber 1, thermal insulator of 3cm-thickness, neutron shielding of 16cm-thick Boron paraffin, temperature regulated water at the RT±0.1°C, and for the chamber 2, the temperature regulating unit including the heater of 2kw and the cooler of 1kw, and the water-stream temperature regulated at the RT±0.1°C.

With this system, the temperature was really measured at the RT±0.01°C during 24hrs, and the noise was measured 1 count per 100 seconds closing the shutter.

Fig. 2. Temperature-, Noise-, Vibration-Regulating System at PNO.
NEUTRON INTERFEROMETER

A perfect-crystal neutron interferometer (IFM) was constructed and experimentally performed in 1974 by H. Rauch et al.\(^{[1]}\). There, successive Laue case diffractions were used for the beam handling, hence it is conventionally called LLL-IFM. It has stimulated a great deal of new investigations, more or less in the more fundamental and more applied physics. The following investigations with LLL neutron IFM were performed: precise measurements on the scattering length\(^{[2]}\), the gravitational effects\(^{[3]}\), coherence\(^{[4-5]}\), Fizeau effects\(^{[6]}\), Spin-superposition\(^{[7]}\), complementarity\(^{[8]}\), and post-selection effects\(^{[9]}\). A number of excellent articles of the IFM with perfect crystal were already published, e.g., first ten years of the X-ray interferometer\(^{[10]}\), first collective book on neutron interferometry\(^{[11]}\), neutron interferometer\(^{[12]}\), recent proceedings of "Matter Wave Interferometry"\(^{[13]}\).

Neutron interferometry have been developed steadily in Japan as well\(^{[14-16]}\). We designed and fabricated a large LLL-IFM. The width, the height and the thickness of each plate are 70mm, 40mm and 1.8mm, respectively. The distance between neighboring plates is about 35mm. This IFM was characterized by X-rays, installed as neutron IFM to JRR-2 in JAERI, and gave good performances\(^{[17]}\). Magnetic and nuclear phase shifts were observed recently with the same type of the neutron IFM by our group\(^{[18]}\).

In a conventional neutron IFM, a parallel sided Al-plate is inserted between two plates of the IFM as a phase shifter (Fig. 3). When this plate is rotated with an axis vertical to the beams, it increases or decreases an optical path length and introduces the relative phase shift between two split beams. When the phase shift, \(\phi\), is induced, the intensities, \(I_0\) and \(I_H\), of the O- and the H-beams will change, in practice, for O-beam and for H-beam according to

\[
I_0 = I_{osc} \times (1 + C \cdot \cos \phi)
\]

and,

\[
I_H = I_{osc} \times (1 - C \cdot \cos \phi) + I_{0} 
\]

respectively, where \(I_{osc}\), \(I_{0}\), \(C\) and \(\phi\) represent the intensities of the oscillations, certain theoretical background for the H-beam, the contrast of the interference oscillations and the relative phase shift between two split beams. The intensities, \(I_{osc}\) and \(I_{0}\), depend mainly upon the intensity of the incident beam, beam flux by beam cross-section. On the other hand, the contrast, \(C\), depends upon the perfection of the IFM and the experimental conditions.

![LLL-Neutron Interferometer](image)

Fig. 3. Experimental set-up with LLL-interferometer.
The LLL-IFM, which had given good performances previously at JRR-2, was installed to 3G in JRR-3M. The experimental set-up is shown in Fig. 3. An Al-plate of 3mm in thickness was used as the phase shifter. The wavelength was set to 1.5Å, which gives the Bragg angle of 23.0°. As preliminaries, out of phase interference oscillations for O and H beams were measured and are shown with least square fits in Fig. 4, when the beam size was 3×5mm² with a solar slit of 10 min. of arc collimation before the monochromator. While the amplitudes of the oscillations for two beams are about the same, the contrast for H beam seems to be lower than the O beam. Since the oscillations for H beam have certain theoretical background as shown in eq. (2), the contrast reduction for H beam is quite reasonable. The interference oscillations for O beam with higher contrasts have more importance in most cases.

Fig. 4. Interference oscillations for O and H beams with least square fits. The amplitudes of the oscillations for O- and H-beam are almost the same, the intensities for two beams clearly oscillate out of phase, and the contrast for O-beam, 43(2)%, is higher than that for H-beam.

To get interference oscillations with higher contrast, O beam is more important from the theoretical viewpoint. On the other hand, since the direct beam with inevitable neutrons of higher energy passes near and parallel to the O beam, the shielding for the O detector from the incident beam is significant. We set a slit with B₄C plates before the detector, and reduced the background. The background for O-detector in measuring the interference oscillations was around 0.1 count/s. Typical interference oscillation for O-beam with least square fit is shown in Fig. 5, when the beam cross section was 8×8mm². The contrast of 37.4(5)% and the amplitude of the interference oscillation of 4.657(10) counts/s were obtained. This intensity is in the same order of that at MURR in USA where many investigations with LLL-IFM are having been made[5,6,9].

Fig. 5. Typical interference oscillation for O-beam with least square fits when the beam size is 8×8mm². The counting rate of the amplitude of oscillation was 4.657(10) counts/sec, which was the same order of that at MURR in USA.
Interference oscillations with various beam size were measured as well. The counting rates of the amplitude and the contrasts of each interference oscillation for O-beams are shown in Table 2 with horizontal by vertical beam sizes. High contrast oscillations remained even with large beam sizes, which shows that the IFM used here was well fabricated. Since some solar slits are equipped before the monochromator at 3G, we changed to fine one of 10 min. of arc collimation and the interference oscillation was measured. Best contrast of 43(2)% was obtained, but the counting rate was reduced to 0.64(3) count/s.

### Table 2: Amplitudes and Contrasts of Interference Oscillations with Various Beam Sizes

<table>
<thead>
<tr>
<th>Beam Size (HeV/cm²)</th>
<th>Amplitude (cpm)</th>
<th>Contrast (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 × 5</td>
<td>1.306(2)</td>
<td>36.1(7)</td>
</tr>
<tr>
<td>5 × 7</td>
<td>2.739(7)</td>
<td>33.8(11)</td>
</tr>
<tr>
<td>6 × 10</td>
<td>4.478(9)</td>
<td>32.7(8)</td>
</tr>
<tr>
<td>8 × 8</td>
<td>4.657(10)</td>
<td>37.4(5)</td>
</tr>
</tbody>
</table>

**SUMMARY**

Neutron interferometry at 3G in JRR-3M was demonstrated, where the best contrast of 43%, or the counting rate of the amplitude of the interference oscillation of more than 4.6 count/s was obtained. Further improvements for higher contrast can bring more counting rate of the amplitude of the oscillations. It is feasible to perform the neutron interferometry at 3G with advantages of wavelength-variable and low background double crystal monochromators, the equipment for the constant temperature control with high accuracy, and the compact and small detector shield with low background. We are planning to perform further neutron interferometry, e.g., new neutron IFM with separated two perfect crystals which will bring a new flavor to a neutron interferometry.

**REFERENCES**

JRR-3M NEUTRON RADIOGRAPHY FACILITY

Akira TSURUNO, Masahito MATSUBAYASHI

Department of Research Reactor
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 JAPAN

ABSTRACT

In March 1991, the new neutron radiography facility was completed in JRR-3M. From the result of the characteristic measurements, JRR-3M Neutron Radiography Facility is proved to have very excellent quality in respect of neutron flux, n/\gamma ratio and collimator ratio.

JRR-3M Neutron Radiography Facility consists of the thermal neutron radiography facility (TNRF 1, 2) and the cold neutron radiography facility (CNRF).

TNRF 1 is for examinations of high activated materials, such as spent fuels. TNRF 2, which is located behind TNRF 1, is for conventional non-destructive inspections. CNRF uses cold neutron beam through the cold neutron guide tube from cold neutron source.

Introduction

The JRR-3M was upgraded after twenty-one year operation in 1990. And a renewal of JRR-3M Neutron Radiography Facility followed the modification of JRR-3 in 1991. Advantages of JRR-3M Neutron Radiography Facility are multiple usage, high neutron flux, availability of many kinds of neutron radiography techniques and ability of choosing neutron energy.

The description and the design of this facility before the completion were already reported.1, 2 This report presents the introduction of JRR-3M Neutron Radiography Facility and the results of characteristic measurement.

Facility Description

A layout of JRR-3M Neutron Radiography Facility is shown in Fig. 1. This facility consists of the Thermal Neutron Radiography Facility (TNRF) and the Cold Neutron Radiography Facility (CNRF). TNRF is installed at the horizontal beam tube, TR, in the JRR-3M reactor hall. CNRF is installed at the end of cold neutron guide tube, C2-3, in the guide hall of the experimenter building.
Fig. 1 Layout of JRR-3M Neutron Radiography Facility

Thermal neutron beam

Thermal neutron beam for TNRF is taken from 30 mm square aperture of the horizontal beam tube (7F). The maximum thermal neutron flux in the heavy water tank is about $2 \times 10^{14}$ n/cm$^2$/s. This beam tube is arranged tangentially to the core to reduce $\gamma$ ray and fast neutrons in the neutron beam. This neutron beam is collimated by the boron-nitride lined divergent pyramid aluminum tube followed by the beam shutter. This thermal neutron collimator supplies TNRF with more than $1 \times 10^{9}$ n/cm$^2$/s neutron beam. The horizontal section of the collimator is shown in Fig. 2.

Fig. 2 Thermal neutron collimator
Cold neutron beam

Cold neutron beam is taken from the cold neutron source (CNS). CNS converts thermal neutrons in the heavy water tank to cold neutrons with liquid H₂ at 20° K. The cold neutron beam for CNRF is led through the cold neutron guide tube (C2-3). This guide tube supplies CNRF with more than 1 x 10¹⁵ n/cm²/s neutron beam. This cold neutron beam is almost parallel and low γ-ray contained but narrow. And its characteristic wave length is 0.4 nm. The beam size (section size of the inner guide tube) is 20mm x 50mm.

Thermal neutron radiography facility

TNRF has two radiographing rooms. One (TNRF 1) is prepared for non-destructive inspections of high activated materials. The other (TNRF 2) is prepared for ordinary non-destructive inspections. TNRF 2 is set behind TNRF 1. Because they share the 7R thermal neutron beam as a neutron source, they cannot be used at the same time. Each radiographing room can be used by switching the collimators. A cross section of TNRF is shown in Fig. 3.

![Diagram](image)

**Fig. 3** Thermal neutron radiography facility

TNRF 1

TNRF 1 is depicted on the left of Fig. 3. This room is typically used for post- and mid-irradiation examination of high activated materials. The inner room size is 900mm wide, 1.400mm long and 1.850mm high. The acceptable capacity of radioactivity is 370TBq. This value is estimated as the radioactivity of a spent nuclear fuel. Because of high radioactivity of materials, the room is enclosed with thick shielding walls. They are composed of 400mm thick steel and 150mm...
thick boron mixed polyethylene.

High activated materials, such as spent nuclear fuels and irradiated capsules, are put into the room through its roof port by the transfer cask. A spent nuclear fuel element of 140mm in outer diameter and 1,100mm in full length is acceptable. In this room, transfer method (converter: 0.1mm Dysprosium foil) is used to take radiographs of materials which contain high γ ray source or are strongly activated. The converter are inserted into the room and are close contact with material by the cassette handling device. This room is equipped with the collimator switching mechanism, the sample holder and the cassette handling device.

TNRF 2

TNRF 2 is depicted on right of Fig.3. The inner room size is 800mm wide, 2,000mm long and 1,850mm high. This room has the entrance with a shielding door and a 1m x 1m roof hatch. Experimenters can enter the room through the entrance and set materials by hand. In case of heavy materials, they also can be carried into the room through the roof hatch using the crane. Thermal neutrons come from the hole in the back wall of TNRF 1. This room is equipped with the shutter, the sample table, the boron nitride shutter and the neutron television system (NTVS). This NTVS is composed of a fluorescent converter, a mirror and a high sensitive television camera in the dark box. NTVS can make real-time non-destructive inspection available in this room. In addition, NTVS is connected to the personal computer, which is able to do the Neutron Computed Tomography.
Cold neutron radiography facility

A cross section of CNRF is shown in Fig. 4. The inner room size is 900mm wide, 1,400mm long and 1,000mm high. This facility is equipped with the beam shutter, the sample table and the neutron television system (NTVS). This NTVS, similar to that of TNRF 2, makes real-time non-destructive inspections available. However the beam size is too narrow (20mm x 50mm) to observe large materials on real-time. Dynamic image integration using the image processor make the observation of wider materials than beam size available.

The utility time at C2-3, where CNRF is installed, is shared with four experimenter groups. Therefore CNRF is designed as a movable box type apparatus.

Neutron Radiography Techniques

many neutron radiography techniques can be used in JRR-3M Neutron Radiography Facility.27

Static neutron radiography

The two prime methods employed are Direct Exposure Method and Transfer Exposure Method. A gadolinium vapor deposited screen (25μm thick) and Kodak SR X-ray film with a vacuum cassette is used in Direct Exposure Method. By this method, highest resolution radiographs can be taken. Direct Exposure Method is mainly used in TNRF 2 and CNRF. Static images from NTVS with Cooled-CCD TV camera and Full-color digital printer are under installation.

Transfer Exposure Method is intended only in TNRF 1 for high activated materials. After 0.1mm thick dysprosium foil is exposed, the latent image is transferred to usual X-ray film in a vacuum cassette. Also Track-etch Method is available.

Dynamic neutron radiography

Particular advantage of TNRF 2 is availability of 255mm x 305mm beam field with high thermal neutron flux. It makes dynamic imaging of relatively large material possible. Some of the examples are the imaging of DNB (Departure from Nucleate Boiling) phenomenon which was carried out in conjunction with Heat Transfer and Fluid Flow Laboratory, JAERI43 and the observation of two-phase flow in a bent heat pipe in conjunction with Nagoya University51. For dynamic imaging, fluorescent converter is used coupling with Silicon Intensifier Target tube. Two fluorescent converters, 6LiF-ZnS(Ag) and GdO2S(Tb), are available. The images are viewed on TV monitor and are recorded on a video tape, which gives a frame repetition rate of 30 frames/second on Video printer.

Computed tomography (CT)

The high grade image processor is installed in the image processing room at the Research Reactor Experimental Manage Building. The images of films or video tapes are processed in this room. In near future we have the data transfer from
TNRF to the image processing room by the light fiber cable.

CT, one of the image processing, is carried at TNRF 2 by the personal computer (PC). PC controls the turn table, on which the sample is set, and takes projection data of the sample from each angle of full rotation or half rotation. After taking projection data, PC calculates these data for reconstruction of the image using the transputer. The tomographic image is displayed on the TV monitor by 512 x 512 pixels. Filtered back projection method with Ramachandran-Lakshmiremanan filter is used for the reconstruction algorithm.

Dynamic image integration

Above-mentioned, the beam size in CNRF is too narrow. So we must use the Dynamic Image Integration using the image processor for large materials. By this method the sample images shift horizontally through the slit-type narrow beam, and are integrated in the memory with the sample position. This function enables to generate the over all sample image from the partial images under the slit-beam. Consequently, the image of sample, crossing through the slit-beam, appears at the left side on the TV monitor and shift to the right side as the sample moves.

Characteristics of JRR-3M Neutron Radiography Facility

The characteristics of JRR-3M neutron radiography facility are shown in Table 1. Gold foils were used for the measurement of neutron flux, and 0.5 mm thick cadmium plate covers for measurement of Cd ratio. Thermo luminescence detectors (TLDs) with fluoride lithium (LiF) capsules, which eliminate an effect of neutrons. were used for the measurement of X-ray dose equivalent.\(^6\)

Table 1 Characteristics of JRR-3M Neutron Radiography Facility

<table>
<thead>
<tr>
<th>Facility</th>
<th>Neutron flux (n/m^2\cdot s)</th>
<th>Cd Ratio</th>
<th>(n/\gamma) (n/cm^2\cdot\mu Sv) (\text{Sv/h})</th>
<th>Collimator ratio (L/D) *2</th>
<th>Radiographic Field size (W\times H\times t)</th>
<th>Sample size (\text{kg})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNRF-1</td>
<td>(2.6 \times 10^8)</td>
<td>81</td>
<td>(5417) (41) (5492) (48)</td>
<td>(132) (114)</td>
<td>(115 \times 432)</td>
<td>(960 \times 130)</td>
</tr>
<tr>
<td>TNRF-2</td>
<td>(1.5 \times 10^8)</td>
<td>130</td>
<td>(62.5) (2.16) (7277) (41) (7352) (48)</td>
<td>(176) (153)</td>
<td>(225 \times 305)</td>
<td>(400 \times 400 \times 500)</td>
</tr>
<tr>
<td>CNRF</td>
<td>(2.3 \times 10^8)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>(20 \times 50)</td>
<td>(400 \times 400 \times 600)</td>
</tr>
</tbody>
</table>

*1 Combination of Gd converter and SR film, \(4 \times 10^3 \text{n/cm}^2\cdot\text{Sv} = 1\)
*2 Collimator ratio in TNRF 1 are calculated values using the measured values in TNRF 2 with geometrical correction.
As a result, neutron fluxes are above $1 \times 10^{6}$ n/cm²/s at the sample position in both TNRF and CNRF. These values are about ten times higher than the neutron fluxes in the other facilities in Japan. This improves the quality of dynamic imaging of moving samples. The Cd ratios, measured in TNRF 1 and 2, were 81 and 130 respectively. It indicates good thermalization. The γ ray dose equivalent was measured only in TNRF 2, and was 2.16 Sv/h. When the direct exposure method with gadolinium converter and SR film, n/γ ratio is 62.5. In this combination, the best exposure time is about 20 seconds.

The collimator ratios, measured in TNRF 2 by Kobayashi's method[7], were 175 in the vertical direction and 153 in the horizontal direction. This guarantees high resolution of radiographs.

**Conclusion**

After characteristic measurements, it was confirmed that the JRR-3M neutron radiography facility is one of the leading neutron radiography facility in the world. Both of the thermal neutron flux and the cold neutron flux are above $1 \times 10^{6}$ n/cm²/s. The collimator ratio is over 100, and the n/γ ratio is very high.

Various kinds of applications to the JRR-3M Neutron Radiography Facility are hoped in future.

**References**

NEUTRON RADIOGRAPHY RESEARCH ACTIVITIES AT KURRI

Shigenori FUJINE, Kenji YONEDA and Keiji KANDA

Research Reactor Institute, Kyoto University (KURRI)
Kumatori-cho, Sennan-gun, Osaka 590-04, Japan

ABSTRACT

The radiography facility for thermal neutron has been installed at the E-2 experimental hole of the Kyoto University Reactor (KUR) since 1974 and provided good characteristics.

To observe a dynamic event and to test many samples, the real-time neutron radiography (i.e. neutron television – NTV) system has been introduced to this facility since 1980 and practically applied to various applications with image processing techniques.

Recently a cold neutron beam hole (CN-2) has been available at the graphite column and preliminary radiographic tests were tried.

In this paper, these neutron radiography systems and brief explanations for some of applications at KURRI are described.

INTRODUCTION

At KURRI, neutron radiography has been researched since 1974. The KUR neutron radiography facility is installed at the E-2 experimental hole\(^1\) and has the excellent characteristics. To observe dynamic phenomena and to test many samples quickly, the real-time neutron radiography system was introduced in 1980\(^2,3\).

The NTV system has been practically applied to penetrating the side plates containing boron burnable poison to test MTR type fuel, to investigation of moving objects\(^4,5\), to neutron computed tomography (NCT)\(^6,7\), to visualization of particles motion in a spouted bed\(^8\), and to visualization and analysis on air–water two–phase flow\(^9,10,11\).

A cold neutron beam hole has been available for neutron radiography at the graphite column since 1989 and preliminary radiographic tests were tried\(^12,13\).

The KUR is a joint use research reactor (5MW) for universities and research institutes in Japan. The facility is also used to study for graduated students\(^14,15\) and overseas researchers. Therefore, many researchers have come to use this facility for various applications, for example;

- Standardization for Determining Image Quality\(^16\),
from Department of Nuclear Engineering, Faculty of Engineering, Nagoya University,
the Atomic Energy Research Laboratory, Musashi Institute Technology,
the Institute for Atomic Energy, Rikkyo University,
the Atomic Energy Research Institute, Kinki University,
the Japan Atomic Energy Research Institute (JAERI),
and the Radiation Center of Osaka Prefecture (now: Univ. of Osaka Prefecture),
- Heat Pipe\(^{17}\), Testing of defects in Structural Materials\(^{18}\), Track–Etch Method, Fluid Dynamics\(^{19}\), Testing New Converters\(^{20}\), NCT\(^{21}\), Basic Research on Quantitative Neutron Radiography\(^{22}\), Analysis of Distribution of Hydrogen in Palladium\(^{23}\), from Nagoya University,
- Development of the New Converters (Kasei Optonix, Ltd.)\(^{24}\),
  Test of Imaging Plates (Fuji Photo Film Co., Ltd.)\(^{25}\),
  Application to Archaeological Objects and Fine Arts (Gangoji Institute for Research of Cultural Property)\(^{26,27}\),
  \(^{126}\)Sb–Be Neutrons to CT for Iron Products\(^{28}\), Core Detection in Turbine Blades, Some Parts of a Space Rocket,
from the Radiation Center of Osaka Prefecture (Univ. of Osaka Pref.),
- Accurate Measurements of Characteristics Factors at the E–2 Facility,
from the Institute for Atomic Energy, Rikkyo University,
- Visualization and Analysis of Particles Motion in a Spouted Bed\(^{8}\),
from Department of Chemical Engineering, Faculty of Engineering, Kyoto University,
- Investigating Ceramics Structure to the Minutest Details,
from Department of Material Science, Faculty of Engineering, Tottori University,
- Preliminary Experiment Using Cold Neutrons\(^{29,30}\),
from the Institute for Atomic Energy, Rikkyo University,
Nagoya University, University of Osaka Prefecture and JAERI.

Some researchers of KURRI also have the joint researches in this field at the "YAYOI" Fast Neutron Source Reactor, University of Tokyo\(^{31,32,33}\),
the Institute for Atomic Energy, Rikkyo University,
the Atomic Energy Research Laboratory, Musashi Institute of Technology,
the JRR–3M, Japan Atomic Energy Research Institute (JAERI),
the Nuclear Safety Research Reactor, JAERI,
and the Atomic Energy Research Institute, Kinki University.

The main subjects of research in progress are visualization and analysis on air–water two–phase flow, construction of the image data base system on neutron radiography, applications using cold neutrons and development of NTV system with high sensitivity and high resolution for fast and cold neutrons.

This paper describes the KUR neutron facilities and brief explanations for some of above applications.

**THERMAL NEUTRON RADIOGRAPHY FACILITY**

The KUR thermal neutron radiography facility has been installed at the E–2 experimental hole, which faces the heavy water tank (Fig. 1) and can produce thermal neutron flux with
high quality for neutron radiography. It was originally prepared for use to thermal irradiation experiments, and for neutron radiography use there were some problems, such as the need for collimator for better image quality and reducing the release of radioactive $^{41}$Ar, and so on.

A divergent collimator of 5 cm input diameter (D) and 500 cm length (L) was used and the part of the collimator in the $E=2$ hole was in an aluminium plug to prevent the release of radioactive $^{41}$Ar. As a gamma ray filter, bismuth 1 cm thick was placed in the Aluminum plug and a neutron shutter ($B_4C$) was used at approximately the middle of collimator. The thermal neutron radiography facility is shown in Fig. 2.

![Figure 1. Horizontal View of the KUR Experimental Holes.](image1)

![Figure 2. The KUR Thermal Neutron Radiography Facility.](image2)
After preliminary experiments to resolve these problems, the facility provided the following advantages;

1. high neutron flux at the film position \((1.2 \times 10^6 \text{ n/cm}^2\text{-sec})\),
2. large Cd ratio measured with a gold foil \((400)\),
3. low gamma ray dose rate \((4.2 \text{ R/h})\),
4. Large n/\gamma ratio \((10^6 \text{ /cm}^2\text{-mR})\),
5. large exposure are \((16 \text{ cm in dia.})\),
6. large collimation ratio \((L/D 100)\).

These characteristics are summarized in Table 1.

As a converter for the film method, the gadolinium (Gd) converter with a vacuum cassette has been generally used with the highest resolution. Many commercialized intensifier screens for X-ray use, based on Gd_2O_2S(Tb) such as KH, KO-500, KO-750, G-4 and G-8, are available with high sensitivity, and also can be used for electronic imaging.

Using a Gd direct film method with ASTM-75 and RISØ-81 Image Quality Indicators, NCSR values are satisfied 75-15-10 with ASTM-75; i.e. thermal neutron content 85 %, scattered neutron content 12 %, resolution indicator 11 and Category I (NCHG=65-6-6) with RISØ-81 is also satisfied; 79-7-7. Using KO-500B converter with SR film, NCSR values are 98.9 %, 8.8 %, 11 and NCHG values are 92.8 %, 7, 7.

Table 1. Characteristics of the KUR Thermal NRG Facility.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Reactor / Power</td>
</tr>
<tr>
<td>2</td>
<td>Peak (\phi\text{th}) in core</td>
</tr>
<tr>
<td>3</td>
<td>Range of L</td>
</tr>
<tr>
<td>4</td>
<td>Standard L / D</td>
</tr>
<tr>
<td>5</td>
<td>(\phi\text{th}) at film</td>
</tr>
<tr>
<td>6</td>
<td>Gamma dose rate</td>
</tr>
<tr>
<td>7</td>
<td>Cadmium ratio</td>
</tr>
<tr>
<td>8</td>
<td>Neutron/Gamma ray ratio</td>
</tr>
<tr>
<td>9</td>
<td>Film size available</td>
</tr>
<tr>
<td>10</td>
<td>Beam uniformity</td>
</tr>
<tr>
<td>11</td>
<td>ASTM-75 specification</td>
</tr>
<tr>
<td>12</td>
<td>ASTM(RISØ)-81 (NC-H-G)</td>
</tr>
</tbody>
</table>

COLD NEUTRON RADIOGRAPHY FACILITY

A cold neutron beam hole (CN-2) has been available at KURRI since 1989. The cold neutron source was installed in the graphite thermal column as shown in Fig. 1. The layout of cold neutron guide tube is shown in Fig. 3\(^{(12,13)}\). The characteristic wavelength is designed to be 2.6 Å. The imaging area is 10 mm (in width) x 74 mm (in Height) and the cold neutron flux is expected \(1 \times 10^7 \text{ n/cm}^2\text{-sec} (>3 \text{ Å, at the exit of CN-2 guide tube})\). The image can be obtained by scanning a film in the cassette with fluence of about \(10^9 \text{ n/cm}^2\).

The preliminary experiments are presented in detail in references\(^{(12,13)}\). In the near future, CN-3 beam hole in Fig. 3 will be arranged for neutron radiography.
REAL-TIME IMAGING SYSTEM

A block diagram of KUR NTV system is shown in Fig. 4. A neutron radiographic image is directly taken from a neutron converter screen with a high sensitive camera (Image Orthicon tube or Silicon Intensifier Target (SIT) tube camera) without image intensifier.

The images from the TV system are digitized through the high speed video analog–digital converter (ADC) (1/30 sec/frame). The digitized images with pseudo color have resolution of 512 x 480 pixels, 256 gray scale and with a DMA interface (TVIP–4100–II). The digital images are fed to an image processing system and a high performance personal computer is connected with an interface.
APPLICATIONS OF NEUTRON RADIOGRAPHY

Visualization on Gas–Liquid Two–Phase Flow\(^{6,10,11}\)

The neutron radiography technique was introduced to visualize a gas–liquid two–phase flow in metallic duct, and measure the void fraction with use of image processing technique. The experiments were performed using the neutron radiography facilities at the E–2 hole of the KUR, the Nuclear Safety Research Reactor (NSRR) and the JRR–3M of JAERI.

The neutron radiography system produced video images with enough quality to delineate flow regimes. The average void fraction obtained with image processing technique agreed well with optical method and the conductance probe method. The relation between gas velocity and mixture volumetric flux was compared with the drift correlation. The agreement was good for wide liquid velocity range.

In the near future, it is expected to be able to calculate the interfacial area concentration with better quality images taken at the JRR–3M.

Some parts of these works were supported by the Grant–in–Aid for Scientific Research (A) from Ministry of Education, Science and Culture (1986–1987, 1989–1990).

This work is presented at this symposium (poster session #405), entitled "Visualization and Measurement of Fluid Phenomena Using Neutron Radiography Techniques" by K. Mishima et al.

Study of Liquid–Solid Two–Phase Flow\(^6\)

Motion of solid particles in a spouted bed was visualized by using neutron radiography. Trajectories and velocity profiles of particles in annular region were obtained from the radiography. Result indicates that both the trajectory and radial profile of particle velocity normalized by mean velocity of fluid through nozzle are almost independent of height of packing and Reynolds number.

The profiles of packed density in a spouted bed were also investigated by neutron radiography and the availability of neutron radiography has been confirmed.

This work was supported by the Grant–in–Aid for Developmental Scientific Research from the Ministry of Education, Science and Culture (1990–1991).

International Cooperative Research Program

The Research Reactor Institute, Kyoto University and the Phoenix Memorial Laboratory (PML), the University of Michigan agreed to Memorandum to Promote Academic Cooperation and Exchange in November, 1987.

In the Memorandum it is written, "In order to facilitate academic cooperation and exchange in scientific and technical development on research reactors, their uses and related subjects, they will encourage in particular activities: all those activities shall be aimed exclusively at peaceful uses: (1) The exchange of research publications. (2) The exchange of researchers, technicians and students. (3) Joint research meetings. (4) Joint research. (5) Research by mutual use of facilities."

The joint research program was supported for three years by the Grant–in–Aid for International Scientific Research Program: University–to–University Cooperative Research from the Ministry of Education, Science and Culture (1990–1992).

At KURRI various applications have been studied by using the KUR and at the University of Michigan, PML, neutron radiography has also been used in the lubrication studies, spray
patterns and spray dynamics, several phenomena in porous media, computer reconstructed neutron tomography, fluid flow studies, and structure and foreign material applications. As the preliminary experiment for this program, visualization of air–water two-phase flow in a small diameter tube and a narrow rectangular duct was considered in 1991 and 1992. The various images of two-phase flow (bubbly, slug, churn and annular) were obtained with a LIIXI NID system and an EMI system at PML. These images were improved by beam correction and averaging technique using Quantex QX–9200 image processing system. The images were sufficiently clear for observation of flow condition and it is expected the quantitative research on two-phase flow follows, such as the measurements void fraction and rising velocity of bubbles. The feasibility of this study could be succeeded to a future program.

At present, neutron radiography has been used to inspect coking and foreign materials in a gas turbine engine nozzle.

Development of Imaging Techniques for Fast Neutron Radiography (FNR)

Since 1986, researchers from various organizations frequently gathered at the YAYOI reactor and carried out the experimental program of fast neutron radiography. The YAYOI reactor is one of fast neutron source reactor for research purpose and an average energy of the neutron beam is estimated to be about 0.8 MeV and applicable to FNR. The neutron fluxes at the exit of the beam holes were measured to be $10^5 - 10^7$ n/cm²·sec (>1.3 MeV at 2 kW operation), and were expected to be able to apply to FNR. In the research programs, imaging techniques were successfully developed using not only CR–39 track detector for a direct imaging but also a fluorescent converter for an electronic real time imaging and for a film method.

Cold Neutron Radiography

Output intensities of the cold neutron guide (CN–2) of KUR–CNS (Cold Neutron Source) were measured with neutron radiographic method. The intensity profiles of the cold neutron beam at various positions in front of the exit of CN–2 were radiographed and quantitatively measured from film optical densities. For the cold neutron source with liquid deuterium moderator, the peak intensity of the CN beam of the CN–2 was measured to be $1.1 \times 10^7$ n/cm²·sec as 'thermal neutron intensity equivalent'. By using the CN beam, CN radiography was carried out with a scanning method of the imaging system. The images with high quality were obtained.

Spatial intensity profiles of a CN beam were measured about the CN–2 guide tube after passing through Be filters as a function of the Be thickness with use of an NR technique. Relative intensities of low energy cold (<5 meV) and high energy cold (5–12 meV) neutron components were analyzed along a horizontal axis on a section in the beam section.

Beam quality dependence regarding with effective total macroscopic cross sections was measured for Pb, Fe and Ti at the KUR (E–2, CNS), the JRR–3M (7R, CNS) and the Rikkyo Reactor.

CONCLUSION

KUR NR facilities and some of applications were presented. KUR NR facilities have
enough characteristics for the film method. The NTV system also is sufficient for the stationary and moving samples, and has been used to various applications. The facilities are expected to use to further applications in the wider fields.

REFERENCES

NEUTRON IMAGING OF MICE AND RATS IN VIVO WITH JRR-3 TNRF

°Gen-ichi MATSUMOTO, *Kazuo KATO and °Ken OHARA

°School of Health Science
Fujita Health University
Toyoake, Aichi, 470-11 Japan

*Inazawa Municipal Hospital
Inazawa, Aichi, 492 Japan

ABSTRACT

After the successful commissioning of JRR-3M in 1991, one of the most powerful thermal neutron beam is now available for neutron radiography. In the present, most promising field for application of neutron radiography will be biology and medical science. As the first step for that direction, mice and rats were taken as sample objects. Both of the two methods, normal static imaging and real-time imaging were performed. Some new and important informations relating to the internal structures of these animals could be obtained in vivo.

INTRODUCTION

In neutron static imaging and real-time imaging, the penetrating nature of neutron beam is used to obtain informations relating to the internal structures of test samples. The value of mass attenuation coefficients of hydrogen being very high, it is extremely difficult to image animals having normal size. For that reasons, neutron radiography is not utilized frequently for biomedical applications except few special examples.

On the other hand, by using neutron instead of X-ray or gamma-ray, different and complementary informations of objects can be obtained. We challenged this venture utilizing very high neutron beam intensity of JRR-3M.

DESCRIPTION OF THE NEUTRON RADIOGRAPHY FACILITY

The system we used is the TNRF (Thermal Neutron Radiography Facility No. 2) of the JRR-3M reactor at the Japan Atomic Energy Research Institute (Tokai).The description of it was reported by Mr. A. Tsuruno at the 4th WCNR at San Francisco ,1992.
The main features of this facility are:

- **Thermal Neutron Beam Intensity**: $1.5 \times 10^8 \, (n/cm^2 \cdot s)$
- **Cd Ratio of Gold**: 176
- **Size of Irradiation Field**: $255 \times 305 \, (mm)$
- **m/γ Ratio**: $6.25 \times 10^6 \, (n/cm^2 \cdot mR)$

In the case of 0.025 eV neutron, the fluence of 936,000 $(n/cm^2)$ corresponds to 1 $(mRem)$. The thermal neutron beam intensity of $1.5 \times 10^8 \, (n/cm^2 \cdot s)$ at the irradiation position is equivalent to:

$$0.16 \, (Rem/s) = 1.6 \times 10^{-3} \, (Sv/s)$$

The gamma dose at the irradiation position can be calculated from the value of $m/γ$ ratio, that is 24 $(mRem/s)$. We suppose that the neutron real-time imaging of living animals would not be so unrealistic.

Gd vacuum cassette is used for static neutron radiography. The real-time imaging system consists of fluorescent converter (the Kasei Optronics, Ltd, Japan), mirror and SIT tube.

**MATERIALS**

Male ddY mice aged 4 weeks (28–32 g body weight) and male F344 rats aged 2 months (180–200 g body weight) purchased from SLC (Hamamatsu, Japan) were used. Animals were fed standard diet pellets CE-2 (CLEA Japan Co., Tokyo, Japan) and water ad libitum.

**NEUTRON IMAGING IN VIVO**

Neutron real-time and static images of mice and rats were taken at TNRF-2 under chloral hydrate anesthesia with the dose of 40 mg/100 g body weight intraperitoneal injection. Animals were fixed on an aluminum grid board with 2 mm thickness by 1/2 inch wide surgical plastic tape (Transpore, 3M Medical, St. Paul, MN, U.S.A.) and aluminum wire (1 mm dia.).

Animals were exposed with neutron beam for 20 or 30 sec..

**RESULTS**

The real-time imaging data were recorded with VHS video tapes.

Fig. 1 and 2 are the photographs from them. In Fig.1, a series of real-time images from the original video tape were averaged at intervals of 30 frames. Artifact of striped pattern
shown in each image may arise from image reduction to a scale of 1/4 of the originals. In Fig. 2, the series of images were acquired at intervals of 20 frames, with image reduction of 1/2.

Fig. 3 and 4 are static neutron images of mice and rats. Fig. 4-B is the optically enlarged photograph of Fig. 4-A.

By visual inspection, the compact bones in the extremities and the tail were distinguished from the surrounding tissues. The cartilages and bone marrows were visible contrasted with the compact bones. However, the bone of the body trunk such as ribs and vertebral bones were not visible due to high neutron attenuation of the body itself.

The bronchi and lungs in the breast were distinguished from the surrounding organs because of high amount of air in these. The ribs did not disturb the shadow of the lungs as in the roentgenography. The air bubbles in the stomach or in the intestines were visible in the abdomen. Thermal neutron were much less absorbed in the air compared to water, protein and lipids.

Fig. 4B shows the bone marrow clearly.

CONCLUSION

The neutron real-time and static imaging of mice and rats were taken utilizing TNRF-2 of JRR-3M. Some new and important informations could be obtained.

For wider applications, the neutron and gamma irradiation dose should be decreased in near future.

ACKNOWLEDGEMENTS

We express our thanks to Mr. A. Tsuruno and Mr. M. Matsubayashi of the Japan Atomic Energy Research Institute for their kind cooperation.
Fig. 1 Neutron-real time images from the original video tape at the interval of 30 frames

Fig. 2 Neutron-real time images from the original video tape at the intervals of 20 frames
Fig. 3 A static neutron image of mice

Fig. 4-A A static neutron image of a mouse and a rat

Fig. 4-B Optically enlarged photograph of the rat in Fig. 4-A
QUANTITATIVE NEUTRON RADIOGRAPHY USING NEUTRON ABSORBING HONEYCOMB – BASIC RESEARCH AND APPLICATION –

*Kanji TASAKA, **Akira TSURUNO and **Masahito MATSUBAYASHI

*Department of Nuclear Engineering, Nagoya University 
Furo-cho, Chikusa-ku, Nagoya, 464-01 JAPAN

**Department of Research Reactor, Tokai Research Establishment, JAERI 
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 JAPAN

ABSTRACT

This investigation concerns quantitative neutron radiography and computed tomography by using a neutron absorbing honeycomb collimator. By setting the neutron absorbing honeycomb collimator between object and imaging system, neutrons scattered in the object were absorbed by the honeycomb material and eliminated before coming to the imaging system, but the neutrons which were transmitted the object without interaction could reach the imaging system. The image by purely transmitted neutrons gives the quantitative information. Two honeycombs were prepared with coating of boron nitride and gadolinium oxide and evaluated for the quantitative application. The relation between the neutron total cross section and the attenuation coefficient confirmed that they were in a fairly good agreement. Application to quantitative computed tomography was also successfully conducted. The new neutron radiography method using the neutron-absorbing honeycomb collimator for the elimination of the scattered neutrons improved remarkably the quantitativeness of the neutron radiography and computed tomography.

INTRODUCTION

The visualization technique of the distribution of neutron cross section in object such as metal hydride[1,2] by neutron radiography neutron television is very useful for scientific investigation as well as industrial nondestructive testing. However, on the observation of the high scattering cross section object by neutron radiography, scattered neutrons from the object degrade the quantitativeness of the neutron radiographic image due to overlap between purely transmitted and scattered neutrons as shown schematically in Fig.1(a). In the case of the neutron computed tomography, CT value indicates no quantitative information due to the scattered neutron effect[3]. Procedure for one-dimensional remove of scattered neutrons from neutron radiograph was proposed by H. Kobayashi and applied to obtain the neutron removal cross section of matter[4]. This procedure was applied to the neutron computed tomography using neutron television by M. Yokoi[5]. Further development of this method was attempted to extend to the two-
In order to evaluate the observed two-dimensional image of neutron radiography and neutron television more quantitatively, the effects of the (L/D) ratio, divergent neutron beam, and scattered neutron from object should be removed from the image of neutron radiograph by using the hard as well as soft imaging system. An elimination method of the effect of the scattered neutrons was proposed and developed by using boron nitride and gadolinium honeycomb collimators\(^7,8\). This investigation concerns to extend the effectiveness of the honeycomb collimator for the television neutron radiography and computed tomography.

**HONEYCOMB COLLIMATOR\(^7,8\)**

As shown in Fig.1(b), a honeycomb collimator which was made of neutron absorbing material was set between object and imaging system. Scattered neutrons from the object material were absorbed by the honeycomb collimator before reaching the imaging systems such as converter/optical film and converter/television camera. Consequently, the image on the converter was formed by the purely transmitted neutrons through object. This image must be more quantitative than the conventional one as Fig.1(a). But the image of the quantitative neutron radiography contains the image of the honeycomb collimator itself. So the image of the object sample which was overlapped by the honeycomb collimator corresponds to a kind of two-dimensional neutron detection system. However, the elimination of overlapped honeycomb collimator image may be preferred. Specification of the boron nitride coated honeycomb collimator (BNHC) and the gadolinium oxide coated honeycomb collimator (GdHC) used in this study was indicated in Table 1.

**EXPERIMENTS AND RESULTS**

Quantitative Neutron Radiography by Film Method
Experiment of quantitative neutron radiography by film method was conducted using the BNHC and GdHC collimators. Step wedge metal samples (Fe, Al, Pb, Cu) were prepared as standard. The neutron radiography facility at the E-2 thermal neutron beam hole in the Kyoto University Reactor was utilized for the quantitative neutron radiography test. Imaging system consisted of gadolinium converter/Kodak SR film (14-18 minutes exposure) combination. Exposed film was developed under the condition of 25°C and 5 minutes by using the usual film development equipment. Optical film density was measured by using a simple densitometer (SDM) and a 2-dimensional scanner (2DS). Fig. 2 shows the relation between the neutron attenuation coefficient and the total thermal neutron macroscopic cross section. The values of the neutron attenuation coefficient obtained in the present experiment (GdHC/2DS and BNHC/SDM) are in good agreement with the macroscopic
ic cross section data\textsuperscript{9). The published data by Kobayashi method\textsuperscript{4} are in a good agreement with the present results. The present BNHC/SDM data are somewhat low compared to the GdHC/2DS\textsuperscript{9} values because of the rather low neutron absorbing capability of the boron coating honeycomb. And the present data by conventional method were appreciably low compared to those by honeycomb collimator methods due to the scattered neutron effect.

Quantitative Neutron Computed Tomography by Television Method

Experiments on the quantitative neutron radiography and the computed tomography were conducted by using the television method in the thermal neutron radiography facility (TNRF-2) at the JRR-3M (Table 2).

<table>
<thead>
<tr>
<th>Specification of JRR-3M TNRF-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron flux</td>
</tr>
<tr>
<td>Collimator ratio (L/D)</td>
</tr>
<tr>
<td>Cd ratio of gold</td>
</tr>
<tr>
<td>(Neutron/gamma ray) ratio</td>
</tr>
</tbody>
</table>

Fig. 3 shows the typical relations between the neutron attenuation ratio ($\ln(I/I_0)$) and the thickness of the iron step with and without Gd honeycomb collimator. The curves with and without honeycomb collimator show a linear relation in a thickness range from 0 to 2cm. The neutron attenuation coefficient is 0.94cm$^{-1}$ and 0.81cm$^{-1}$ for GdHC and WOHC cases, respectively. The total cross section of iron is 1.12cm$^{-1}$ [9]. This indicates that the influence of the scattered neutrons was appreciably decreased. Using

Fig. 3 Relation between neutron attenuation ratio ($\ln(I/I_0)$) and step wedge thickness of iron with and without Gd honeycomb collimator by neutron television method.
the neutron television system, data set of the neutron radiography projections for the computed tomography were obtained by CT principle as illustrated in Fig.4. The data set was recorded with video tape. The digital images converted from the video were used for the shading correction of the projection images of the honeycomb by making a relation of \((\text{projection of sample with honeycomb})/(\text{projection of honeycomb})\). The normalized projection data were obtained without the effects of the scattered neutrons, beam profile and honeycomb. The reconstruction calculation of the computed tomography from the normalized image data set was done at the Nagoya Computer Center.

![Fig. 4 Schematic view of NR projection for computed tomography.](image)

Fig. 4 Schematic view of NR projection for computed tomography.

Fig. 5 shows typical neutron computed tomography (CT) images of metal cylindrical columns (Cu, Cu-Zn, Ti and Al); a) without Gd honeycomb and b) with Gd honeycomb. CT image with HC contained some artifact due to imperfect elimination of the honeycomb image, compared to without honeycomb. Fig. 6 shows the relation between computed tomography value (CT-value) and total cross section of various metals for with and without honeycomb collimator, obtained by the proposed quantitative neutron radiography method. It reveals clearly that the quantitativensness of the CT-value of with honeycomb is very high.

Advanced Developing System

A digital electronic imaging systems of the cooled Plasma-Coupled Device (PCD) had been developed for improving the image dynamic range. Further development has been just progressing by using a high precision cooled Charge-Coupled Device (CCD) camera. The cooled CCD camera image of metal step wedges with Gd-coated aluminum honeycomb collimator of the
a) CT image of cylindrical metals without honeycomb collimator

b) CT image of cylindrical metals with honeycomb collimator

Fig. 5 Reconstruction images by computed tomography with and without honeycomb collimator
Fig. 6 Relation between computed tomography value (CT-value) and total macroscopic cross section of various metals with and without honeycomb collimator.

Fig. 7 Cooled CCD camera image of metal step wedges with Gd-coated aluminum honeycomb collimator.
preliminary test was shown in Fig. 7[12]. In order to eliminate the image of the honeycomb collimator, on the other hand, a micro-honeycomb collimator is now developing by gadolinium coating of ceramics micro-honeycomb with capillary diameter of 6 microns and length of 500 microns. By combining the micro-honeycomb collimator with the two digital imaging devices above-mentioned, highly quantitative neutron radiography and computed tomography systems will be established in very near future.

CONCLUSION

Through this investigation, following conclusion was obtained. A new quantitative neutron radiography and computed tomography by using a neutron absorbing honeycomb collimator has been proposed and verified experimentally. Boron nitride and gadolinium coated aluminum honeycomb collimators were fabricated and applied experimentally for the elimination of the scattered neutrons from the object materials. The attenuation coefficients and computed tomography (CT) values of various materials are evaluated to be consistent with the macroscopic cross section. This indicates that the new neutron radiography method using the neutron-absorbing honeycomb collimator for the elimination of the scattered neutrons improves the quantitativeness of the neutron radiography and computed tomography.

REFERENCES

2) M. Tamaki et al., 3rd Int. Conf. on Cold Fusion, Nagoya, Japan (1992.10), (in print).
VISUALIZATION AND MEASUREMENT OF FLUID PHENOMENA USING NEUTRON RADIOGRAPHY TECHNIQUES

Kaichiro MISHIMA, Takashi, HIBIKI, Shigenori FUJINE, Kenji YONEDA, Keiji KANDA, Hideaki NISHIHARA,
*Akira TSURUNO, *Masahito MAISUBAYASHI,
©Makoto SOBAJIMA and ©Shoichi OHTOMO

Research Reactor Institute, Kyoto University
Kumatori-cho, Sennan-gun, Osaka, 590-04 Japan

*Department of Research Reactor, and
©Department of Nuclear Fuel Safety
Tokai Research Establishment
Japan Atomic Energy Research Institute
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

This paper presents some of the results from recent work performed on the application of neutron radiography to visualization and measurement of fluid phenomena at the Research Reactor Institute of Kyoto University. Experiments have been performed on the following subjects with use of the NR systems at the Japan Research Reactor 3 and the Nuclear Safety Research Reactor of the Japan Atomic Energy Research Institute as well as the Kyoto University Research Reactor: air-water flow in rectangular ducts with 1.0 and 2.4 mm gaps, air-water flow and steam-water flow in a round tube with 4.0 mm inner diameter. The void fraction was measured by processing the images taken by the neutron radiography. The effect of several corrections in image processing was also discussed previously. It was shown that the proposed method could be useful in observing the flow regimes and measuring the void fraction of gas-liquid two-phase flow in narrow channels.

INTRODUCTION

The attenuation characteristics of thermal neutrons indicate that NR is suitable for visualizing a hydrogenous material in a metallic vessel. An electronic imaging (EI) technique, which is one of applied techniques of NR, could produce real-time images of fluid phenomena. Taking advantage of this, some researches have been already performed. Typical studies are (a) high speed photography of a steam-water flow using a TRIGA reactor1, (b) visualization of a two-phase flow in a heat pipe2, and a heated stainless steel tube3, (c) observation of moving behavior of an object in water4, and (d) visualization and void-measurement of air-water flow in a narrow rectangular duct5.

At the Research Reactor Institute of Kyoto University (KURRI) various applications of thermal neutron radiography (NR) have been investigated by using the NR system of the Kyoto University Research Reactor (KUR). In the last several years, much effort has been made to study the feasibility of
quantitative measurement of fluid phenomena by using the EI technique\(^5\)-\(^10\). Particularly, the characteristics of two-phase flow in a narrow flow channel have lately attracted considerable attention related to cooling of the blanket of a fusion reactor and the core of a high-neutron-flux research reactor which burns plate-type fuels. Conventional methods such as the probe method could not be convenient in a narrow flow channel, because it may disturb the stream too much or may not be stiff enough to stand in the stream, resulting in a significant measurement error. On the other hand, NR can produce images of flow without disturbing the stream. For this reason, the EI technique combined with an image processing technique was applied.

This paper presents some of the results from recent research work performed at KURRI on the application of NR to the measurement of air-water and steam water flows in narrow rectangular ducts\(^6,7,8,9\) and small diameter tubes\(^8,8,10\).

**EXPERIMENTAL**

1. NR Facilities and EI Systems

(1) NR Facilities

The facilities used in the experiments are the Japan Research Reactor 3 (JRR3) and the Nuclear Safety Research Reactor (NSRR) of the Japan Atomic Energy Research Institute (JAERI) as well as the KUR. The KUR and JRR3 are pool-type research reactors and their operating powers are 5MW and 20MW, the neutron flux at the beam port being \(1.2 \times 10^6\text{n/cm}^2\text{s}\) and \(1.5 \times 10^8\text{n/cm}^2\text{s}\), respectively. The NSRR is a TRIGA reactor which can be operated either at a steady power or with a pulse-power. Thermal neutron flux at the beam port is \(8 \times 10^6\text{n/cm}^2\text{s}\) at a steady 200kW operation. At a pulsed operation with 3.06 dollars of reactivity, the neutron fluence is \(1 \times 10^{10}\text{n/cm}^2\) and the half width of a pulse is 7.5 ms. Some of the characteristics of the NR facilities are shown in Table 1.

<table>
<thead>
<tr>
<th>Source</th>
<th>Power [MW]</th>
<th>Flux of Thermal Neutron at Film [n/cm²s]</th>
<th>Cd ratio [-]</th>
<th>L/D [-]</th>
<th>Film Size Available [mm²]</th>
<th>n/γ ratio ([n/cm²/µR])</th>
</tr>
</thead>
<tbody>
<tr>
<td>KUR(E-2)</td>
<td>5</td>
<td>(1.2 \times 10^6)</td>
<td>400</td>
<td>100</td>
<td>160Ø</td>
<td>1.0 (\times 10^5)</td>
</tr>
<tr>
<td>JRR3(No.2)</td>
<td>20</td>
<td>(1.5 \times 10^8)</td>
<td>180</td>
<td>H 176</td>
<td>255 (\times 305)</td>
<td>2.5 (\times 10^5)</td>
</tr>
<tr>
<td>NSRR(NRG)</td>
<td>23,000</td>
<td>(1.0 \times 10^{10}\text{n/cm}^2)</td>
<td>8.7</td>
<td>67</td>
<td>200 (\times 200)</td>
<td>5.0 (\times 10^4)</td>
</tr>
</tbody>
</table>

(2) EI Systems

In Fig.1 the block diagrams of the EI systems in the KUR, JRR3 and NSRR experiments are shown, enclosed by a solid line, a broken line and a dotted line, respectively. In the KUR experiment, the combination of NE426 scintillator (LiF + ZnS(Ag)) and a silicone intensifier target (SIT) tube, Tokyo Denshi Kogyo VC-7000, was employed as the imaging system. Enlarged images were obtained by using a close-up lens. In the case that the original image quality is not clear, the image can be integrated using image memory, AVIONICS IMAGE-Σ. In the JRR3 experiment, the combination of a fluorescent converter, Kasei Opt NR and a TV camera, Hamamatsu C1000-12, was employed. Since a lens controller is attached with this EI system, it is possible to zoom in the image. In the NSRR experiment, the film method as well as the combination of a fluorescent converter, Kasei Opt NR and high-speed video system, Nihon Kodak Ektapro 1000, were employed. Video images can be taken at a speed of 1000 frames per second by using this system.
2. Test Loop

(1) KUR and JRR3 Experiments

The test sections were rectangular ducts and round tubes made of aluminum alloy, the dimensions of which are shown in Table 2. Operating fluids were air and deionized water. The set up of the test rig is shown schematically in Fig.2. The water was circulated by a pump. The air was supplied by a compressor, merged into the water in a mixing chamber, flowed upward, and discharged into the atmosphere through a separator.

<table>
<thead>
<tr>
<th>Dimensions of the</th>
<th>Length</th>
<th>Working Fluid</th>
<th>NR Facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross Section [mm]</td>
<td>[mm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rectangular Duct</td>
<td>s=2.4, w=4.0</td>
<td>1400</td>
<td>air-water</td>
</tr>
<tr>
<td></td>
<td>s=1.0, w=4.0</td>
<td>1400</td>
<td>air-water</td>
</tr>
<tr>
<td>Round Tube</td>
<td>d=4.08</td>
<td>1200</td>
<td>air-water</td>
</tr>
<tr>
<td></td>
<td>d=5.0</td>
<td>200</td>
<td>steam-water</td>
</tr>
</tbody>
</table>

(2) NSRR Experiment

The test sections were a rectangular duct and a round tube made of aluminum alloy (see Table 2). The test rig with the rectangular duct was the same as shown in Fig.2. The test loop with the round tube is shown in Fig.3. The loop was filled with deionized water. A steam-water flow was generated by heating the tube with a sheath heater winded around the tube.

3. Calculation of Average Void Fraction

A calibration sample was made of aluminum alloy and has five gaps (0.5, 1.0, 1.5, 2.0, 2.5, 3.0mm). The gaps were filled with deionized water. First, an image of the calibration sample was taken by NR, translated into gray levels and the relation between the gray level and the thickness of the water layer was obtained after several image corrections to the gray levels are made.9)
In this experiment, the linearity of a calibration curve was within 4%. Next, 255 images of two-phase flow in the test section taken by NR were integrated to improve the accuracy of the void fraction measurement. A frame of the image was divided into 480 (vertically) x 512 (horizontally) pixels, and the gray level in each pixel was specified. Comparing the gray level to the calibration curve, the thickness of water layer in each pixel was obtained and so the void fraction could be calculated.

The image processing method was tested against the conventional probe method for air-water flow in a rectangular duct\(^5\). It was pointed out also that several corrections were needed in image processing which might affect the accuracy of measured void fraction. The corrections for dark current, shading, field intensity fluctuation and electric system drift were discussed quantitatively by Hibiki et al.\(^9\),\(^10\).

RESULTS AND DISCUSSION

1. Visualization of Two-Phase Flow

(1) Air-Water Flow in Rectangular Ducts

Typical images of two-phase flows taken by the KUR-NR system are shown in Fig.4. It can be seen that the image quality was good enough to delineate flow regimes. Typical images of air-water flow taken by the JRR3-NR system are also shown in Fig.5. Figures 5(B) and (C) show images enlarged by a telephoto lens and a camera controller, in which bubbles with about 3.0 mm diameter in the water film (Fig.5(B)) and the shape of a disturbance wave being torn away (Fig.5(C)), can be clearly observed. As the neutron flux at the JRR3 was about 100 times as high as that at the KUR, the image quality by the JRR3-NR system is good enough to observe more rapid phenomena than by the KUR-NR system. Best frozen images of two-phase flow were taken by the film method with pulsed NR at NSRR, as shown in Fig.6. In the figure, (A), (B) and (C) depict a slug flow with small bubbles in the liquid slug, a churn flow and an annular flow, respectively.

![Images of two-phase flow regimes](image_url)

Fig.4 Typical two-phase flow regimes observed by EI system at the KUR.
(2) Air-Water Flow in a Round Tube

Typical images of a slug flow in a round tube are shown in Fig. 7. In this figure, (A), (B), (C), (D) and (E) represent the original image taken at the KUR, the caricature of (A), the original image taken at the JRR3, the caricature of (C) and the integrated image over 255 images taken at the KUR, respectively. Though the detail was obscure because of rapid motion, the existence of the liquid slug can be recognized. A series of motion picture of air bubbles slowly rising in stagnant water are also shown in Fig. 8. The shape of bubbles and their motion are clearly observed.

(3) Steam-Water Flow in a Round Tube

An original image of steam-water flow by using a pulsed neutron beam is shown in Fig. 9. The half width of the neutron pulse was 7.5 ms and the frame interval of the high-speed video was 2 ms. By this EI system, the neutron flux only near the peak was high enough to obtain a clear image. Therefore, only two frames of images per pulsed neutron beam were obtained. Slug flow is observed in these photographs. The position of the top of a slug
Fig.9  Images of flow boiling in a small diameter tube taken by the NSRR-NR.

bubble is indicated by a dotted line in Fig. 9. From the comparison between the positions in Fig. 9(A) and (B), it can be seen that the slug bubble moved slightly upward. From the above results, it is shown that the pulsed NR method is applicable to the measurement of rapid phenomena such as a boiling two-phase flow in a metallic duct.

2. Average Void Fraction

The drift flux correlation obtained by Jones-Zuber\(^11\) for a rectangular duct with a large aspect ratio is given as follows:

\[
v_G = \frac{j_G}{\alpha} = C_0 j + (0.23 + 0.13s/w)(\Delta \rho g w/\rho_L)^{1/2}
\]

(1)

where the distribution parameter \(C_0\) is given by the following Ishii's equation\(^12\) for a rectangular duct:

\[
C_0 = 1.35 - 0.35 (\rho_G/\rho_L)^{1/2}
\]

(2)

The correlation for a slug flow in a round tube is given by\(^12\):

\[
v_G = \frac{j_G}{\alpha} = 1.2 j + 0.35 (\Delta \rho g d/\rho_L)^{1/2}
\]

(3)

Using measured void fraction \(\alpha\) in Eqs.(1) and (3), the experimental data are plotted as a relation between \(j_G/\alpha\) versus \(j\). To verify the image processing method, the drift flux correlation was compared between the void fractions measured by the image processing method and the probe method for a rectangular duct with 2.4mm gap. A good agreement between two methods is shown in Fig.10 where optical means the image processing method. The results for the rectangular ducts are shown in Fig. 11 (A) for 1.0mm gap and (B) for 2.4mm gap.

The result for the round tube with 4.0mm I.D. is shown in Fig.12. In the image processing method, several correc-

---

**Fig.10** Comparison between two measuring methods.
Fig. 11 Drift flux correlation of the void data for rectangular ducts with (A): 1.0 mm gap and (B): 2.4 mm gap.

Fig. 12 Drift flux correlation for a round tube.

Fig. 13 Test of the image processing method for a round tube.

...tions are needed. Hibiki et al.10) discussed the effect of those corrections and checked the method against the gray level distribution for an image of a round tube filled with water. Figure 13 shows a good agreement between the theoretical and the measured gray level profile where \( \beta \) and \( x \) denote the logarithmic gray level and the distance in the radial direction, respectively.

CONCLUSION

Visualization of two-phase flows in narrow rectangular ducts and small diameter tubes made of aluminum alloy was performed by using three NR facilities. The characteristics of two-phase flow could be clearly observed from the images taken by NR. The average void fraction was obtained by employing the image processing technique. It was shown also that the void fraction in the test sections used in the present experiments could be correlated well by the drift flux model.

Part of this work was supported by the Grant-in-Aid for Scientific Research, from the Ministry of Education, Science and Culture (No.02045020).
NOMENCLATURE

C₀: distribution parameter [-], D: diameter of the collimator [m], d: inner diameter of the tube [m], g: acceleration of gravity [m/s²], j: mixture volumetric flux (-j_G + j_L) [m/s], j_G: superficial gas velocity [m/s], j_L: superficial liquid velocity [m/s], L: distance from neutron-inlet of collimator to the film [m], s: gap of the duct [m], v_G: gas velocity [m/s], w: width of the duct [m], α: void fraction [-], Δρ: difference of the densities of two phases [kg/m³], ρ_G: gas density [kg/m³], ρ_L: liquid density [kg/m³]

REFERENCES

COLD NEUTRON RADIOGRAPHY USING LOW POWER ACCELERATOR

Yoshiaki KIYANAGI and Hirokatsu IWASA

Department of Nuclear Engineering, Faculty of Engineering, Hokkaido University, Sapporo, 060 Japan

ABSTRACT

A cold neutron source which can be adopted at a low power accelerator was studied. Time-of-flight radiography using the cold neutron source was performed. It is suggested that time-of-flight cold neutron radiography has possibility to distinguish the materials more clearly than the traditional film method since large contrast differences can be obtained by using digital data of the neutron intensity at different energies from thermal to cold region. Material will be identified at the same time by this method.

INTRODUCTION

Neutron radiography is one of the most useful methods in the non-destructive inspection. So far, thermal neutrons are mainly used. Now, it is desired to inspect thicker materials. There are two ways for the thicker material inspection. One is to use high energy neutrons(1) since at high energy region above around 1 MeV the neutron cross section becomes small. The other is to use cold neutrons since a lot of materials have Bragg cut-off at the cold neutron region where the cross section falls off sharply. We can get photos with various contrast depending on the neutron energy because the change of neutron cross section is different from material to material.

So far, cold neutron sources are mainly installed at high power accelerators for the neutron scattering experiments performed for material science. However, there are many facilities equipped with low power accelerators which can be used for the neutron radiography. Installation of a cold neutron source will increase the usefulness of such facilities. Therefore, a simple and convenient cold neutron source should be developed for the neutron radiography. We describe here a new type of cold neutron source and test experiments of a time-of-flight neutron radiography using the cold neutron source.

EXPERIMENTAL

The electron linac at the Hokkaido University was used as
neutron generator. Figure 1 shows experimental set-up of moderator-refrigerator system. Here, we used the existing refrigerator to cool down the moderator but a more compact refrigerator will be sufficient. The moderator system is shown in Fig. 2. The moderator is a coupled liquid hydrogen moderator with a premoderator. The cold neutron intensity from this type of cold moderator is highest(2). We studied best premoderator material. The candidates are polyethylene and ZrH2 which have nearly the same high hydrogen number density. The size of moderator was 12cm x 12cm x 5cm. The temperature of the cold moderator was about 18k.

The neutron radiography measurements were performed by setting the samples at the end of evacuated flight tube. The flight path length is about 6 m from the cold moderator.

![Diagram](image)

**Fig. 1** Experimental set-up of moderator-refrigerator system.

![Diagram](image)

**Fig. 2** Coupled liquid hydrogen moderator system.
COLD NEUTRON SOURCE

Figure 3 shows the energy spectra from the coupled liquid hydrogen moderator with and without premoderator. The thicknesses of the premoderators were chosen to get the highest cold neutron intensity: 2cm for polyethylene and 3cm for ZrH₂. The spectrum shapes in the cold neutron region does not depend on the premoderator materials. The spectrum from the moderator without premoderator has nearly the same shape as those of others. The cold neutron intensity from the polyethylene premoderator case is larger than the that of the ZrH₂ case. The intensity of the cold neutrons from the ZrH₂ case is about 0.75 times that of polyethylene case in the cold neutron region as shown in Fig. 4.

The reasons of the less intensity from the ZrH₂ premoderator are considered as follows. One reason is that the hydrogen number density of the ZrH₂ becomes lower than that of polyethylene because of packing of the powder. The other, this will be the main reason, is that ZrH₂ does not have effective dynamic modes for slowing down the neutrons below 0.15 eV. This result suggests that to supply the thermal neutrons to the liquid hydrogen as many as possible is important to increase the cold neutron intensity from the coupled liquid hydrogen moderator. We also compared the cold neutron intensity with that from traditional decoupled solid methane moderator. The cold neutron intensity from the coupled liquid hydrogen moderator with polyethylene premoderator was about twice that from the decoupled methane. From these results we decided to use the coupled liquid hydrogen moderator with polyethylene premoderator.

Fig. 3 Energy spectra of neutrons emitted from the liquid hydrogen moderator.

Fig. 4 Intensity ratio between ZrH₂ and polyethylene premoderator cases.
TIME-OF-FLIGHT COLD NEUTRON RADIOGRAPHY

We can get digital data as a function of flight time, namely neutron energy, by the method of time-of-flight. These data enable us to make photographs with a variety of contrast and also to identify the materials included in the samples by using the characteristic change of the neutron cross section. Preliminary experiments have been performed to study the effectiveness of the time-of-flight cold neutron radiography.

(a) Contrast variation
We measured the intensity of neutrons transmitted through the samples at intervals of 3 mm. The samples were arranged one-dimensionally. We chose following materials as the samples which are frequently used in manufactured goods: brass, Al, Pb, Cu, Fe, stainless, polyethylene and wood. The width of samples were 12 mm. Figure 5 shows variation of the contrast at different neutron energies. In Fig.5(a), the polyethylene will be clearly distinguished from others. From

![Image](image_url)

Fig.5 Variation of contrast depending on neutron energy.
the energy dependent contrast wood is distinguished by others, too. The differences among brass, Cu, Fe and stainless are recognized in Fig.5(b). The difference between Al and Pb appears more clearly in Fig.5(c). These results suggest that the cold neutron time-of-flight radiography will be able to distinguish the materials more clearly than the traditional film method.

(b) Material identification
Figure 6 shows examples of macro cross sections of sample materials. There are large differences among them. Figure 7 shows a spectrum of incident neutrons and a spectrum of neutrons transmitted through double layer samples of Fe and brass. We calculated the transmitted neutron spectra by using Fe+Brass

![Graphs showing macro cross sections and time-of-flight measurements for Fe, Brass, Copper, and Brass.](image)

Fig.6 Observed macro cross sections in the low energy region used in the calculation.

Fig.7 Incident and transmission spectra in the case of (Fe and brass) sample. Solid lines are calculated transmission spectra.
the cross sections shown in Fig.6. By fitting the
calculated spectra to the experimental one, we performed the
test of fit with a use of $\chi^2$-test. Figure 7(a) shows the
fitting when using the correct sample. In this case, the value
of $\chi^2$ is 111.55 which is less than a value of significant
level 5 %, 165. Figure 7(b) and 7(c) are examples using the
cross sections of incorrect materials, (Fe, Cu) and
(Cu, brass). The values of $\chi^2$ become very large. Therefore,
the fitting is rejected. We examined other cases using
different materials and all cases examined showed similar
behavior. The results suggest that material identification
will be performed by using the cold neutron transmission
data.

CONCLUSIONS

The cold neutron source proposed is conventional one since
this can be constructed by using the small-sized
refrigerator on the market. This will be useful to get
photographs with different contrast in the film methods, too.
A cold neutron radiography combined with the time-of-flight
method has possibility to give more informations than the
traditional film method.

REFERENCES

2nd International Symposium on Advanced Nuclear Energy
Research (January 24-26, 1990), pp. 614.
(2) Y. Kiyanagi, N. Watanabe and H. Iwasa, Nucl. Instr. Meth.,
Application of Neutron Radiography to Flow Visualization

N. Takenaka, T. Fujii, A. Ono, T. Nakazawa and A. Turuno

Department of Mechanical Engineering
College of Liberal Arts
Kobe University
Rokodai-cho, Nada-ku, Kobe-city, 657 Japan

Department of Power Systems Engineering
Kobe university of Mercantile Marine
Fukae-Minami-machi, Higashinada-ku, Kobe-city, 658 Japan

Department of Research Reactor
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-kenn, 319-11 Japan

ABSTRACT

Flow visualization is a useful method to study thermal hydraulics phenomena which are important in mechanical, nuclear and chemical engineering. When the flow is under high pressure and high temperature conditions or the fluid is a liquid metal, the flow visualization is often difficult by visible rays. Since most of metal are visible by a thermal neutron ray and some elements are quite opaque to it, the neutron radiography can be applied to visualize flows in metallic tubes and containers and flows in a liquid metal. In this study, some methods were developed to visualize multiphase flows in metallic containers and flows in a liquid metal by neutron radiography. Following flows were visualized by real-time thermal neutron radiography system at JRR-3M in JAERI: flows in a liquid metal, gas-liquid two-phase flows in a metallic container, boiling two-phase flow in a heat exchanger for a spacecraft and a fluidized bed in a metallic container. It was shown that the neutron radiography was applicable to the flow visualizations which were difficult by the other methods.

INTRODUCTION

Flow visualization is a useful method to study thermal hydraulic phenomena which are important in thermal, mechanical, nuclear and chemical engineering. The flows with heat transfer or chemical reaction are often multiphase flows which are mixtures of liquid, gas or solid phase. To study the multiphase flow, flow pattern maps are required to analyze thermal hydraulics of multiphase flows and observations of the flow patterns are necessary to understand the mechanism of the multiphase flows for formulating the constitutive equations. Flow visualization of a liquid metal was difficult because a metal is not transparent by visible rays.

Visualization studies have been carried out by many researchers and many visualization techniques have been proposed. The thermal hydraulic
systems may be classified into three cases from a view of the visualization techniques:
1. flows of both the working fluids and the wall of a tube or a vessel are transparent to visible rays.
2. those which can be simulated by the transparent systems, and
3. those in which either the working fluids or the wall is opaque to visible rays and are difficult to be simulated by the transparent systems.

Flows in industrial machines are often included in case 3 as they are made of metal and are often difficult to be simulated by the transparent systems. New techniques have been developed for the flow visualizations of case 3 and some of them are radiography techniques.

Applications of neutron radiography have been proposed for many non-destructive examinations since the attenuation characteristics of neutron ray in materials are much different from those of X-ray and γ-ray, i.e., the image difficult to be visualized by X-ray and γ-ray can possibly be visualized by neutron ray. Many applications have been reported and most of them were presented in the international neutron radiography conferences [1] and its techniques were summarized in a handbook [2]. Some of them are methods to obtain still images on films and others are real-time methods taken by a video camera. The real-time neutron radiography methods are applicable to observe the dynamic behaviors of the flows which are difficult to be observed by the other methods.

**PRINCIPLE OF NEUTRON RADIOGRAPHY ON THE PRESENT APPLICATIONS**

Radiography is a technique to visualize the structure of an object by the difference of the attenuation rate of radio rays to the materials of the object. An X-ray is often used for non-destructive examinations. The mass attenuation coefficients of an X-ray increases with increasing the atomic number of the irradiated material. On the other hand, those of a neutron ray are large for small atomic number elements like hydrogen and for some special elements such as cadmium. They are small for the industrial materials of aluminum and stainless steel and heavy metals like lead and bismuth. Therefore, the neutron radiography is suitable for visualizing the behaviors of water flows in a metallic wall of aluminum and stainless steel. It is also suitable for visualizing flows of lead-bismuth eutectic by tracers and dye which contain cadmium.

**EXPERIMENTS AND PROCEDURES**

Thermal neutron rays from a nuclear reactor was collimated by a duct made of polystyrene to obtain a parallel neutron beam. Then the beam was irradiated to the test object. The radiography image of the object was converted to a visible ray image by a scintillation converter and was recorded by a high sensitivity video camera on the mirror. The recorded images were processed by image processors. The speed of the video camera was 30 frame/sec.

The experimental apparatus was remote-controlled outside of the irradiation room. Tubes for water and gas and codes for electrical inputs and signals, the length of which was about 10 m, were equipped between the irradiation room and the operator room. The water, the gas and the electrical inputs were supplied and controlled from the operator room to the test section and the signals were recorded by a multi-pen recorder and a digital data logger in the operator room.
VISUALIZED RESULTS

Examples of the experimental test sections and the visualized images were shown below:

Figures 1 (a)-(c) show a test section, image processing methods and a vector field of a forced convection flow in the lead-bismuth eutectic. The flow was visualized by tracers, particles about 2mm made of gold-cadmium intermetallic compound, AuCd5, which has a large neutron attenuation coefficient, similar density to the liquid metal and wets well to it. Tracers in the liquid metal which follow the flow can be clearly seen. The test section is a two-dimensional model of a liquid target of a high energy accelerator. The circulation was induced by a bubble pump. The vector field was obtained by a two-dimensional correlation method using two difference images.

Figures 2 (a),(b) show a test section and an image of the solidification of the liquid metal. The molten lead-bismuth eutectic in the container was cooled by water at one side and was solidified. By inserting the solid dye of a lead-bismuth-cadmium alloy which has high neutron attenuation coefficient, similar density to the liquid metal and solvable to it in the liquid phase, the solid-liquid interface was clearly visualized.

Figures 3 (a),(b) show a test section and image processed results of two-dimensional void fraction distribution in a rectangular vessel. Water and nitrogen gas were injected at the lower corner of the vessel and a two-dimensional gas-liquid two-phase flow was formed in the test section. The two-dimensional time-averaged void fraction distributions were obtained by image processing methods, which will be used as benchmark data for two-dimensional simulation codes to predict two-phase flow.

Figures 4 (a),(b) show a test section and a visualized picture of boiling two-phase flows of Freon R-11 in aluminum pipeworks of heat exchangers which is supposed to be used in a spacecraft. The two-phase flow characteristics in the heat exchangers were visualized well.

Figures 5 (a),(b) show a test section and consecutive pictures in a fluidized bed of polystyrene particles in an aluminum container. Bubbling phenomena in the bed were clearly visualized through aluminum wall.

CONCLUSIONS

Liquid metal flows and multiphase flows in metallic container which are important in thermal hydraulics studies were visualized by the neutron radiography. It is shown that the real-time neutron radiography is efficiently applicable to thermal engineering.

REFERENCES

   "Neutron Radiography (3)", Kluwer Pub., 1990

Acknowledgements

The authors wish to express their cordial acknowledgements to Messirs S.Ueda, Y.Motomura and H.Yamano for their aids in the experiment.
Fig. 2(a) Experimental Apparatus for Liquid Metal Solidification by Dye

1. Liquid Metal (Pb-Bi)
2. Electric Heater
3. Heat Exchanger
4. Solid Dye
5. Pump
6. Water Tank
Fig. 4(a) Experimental Apparatus of Thermal Control System for Spacecraft

Fig. 4(b) Visualized Image and Pipe Work
Fig. 5(a) Experimental Apparatus for Fluidized Bed

1. Net
2. Polystyrene Particle
3. Test Section
4. Flow Meter
5. Regulator
6. Nitrogen Gas Bomb

Fig. 5(b) Visualization of Bubbling in Fluidized Bed
Classification of Japanese Granitic Rocks and Clays by K, Ca, Rb, Sr and Its Application to Archaeology

Toshikazu MITSUJI

Laboratory of Physical Chemistry
Nara University of Education
Takabatake chō, Nara city, Nara prefecture
630 Japan

ABSTRACT
In order to develop a scientific method to determine the provenance of the ancient ceramics, an energy dispersive X-ray fluorescence spectrometer made the analysis of Sueki ware, a kind of Japanese ancient ceramics, and granitic rocks. As the result, the elements such as K, Ca, Rb and Sr were found out to be most useful in discriminating kilns. These elements were used to determine the provenance of the earliest sueki. The largest production at that time was carried out in the Suemura, the southern area of Osaka prefecture. The Suemura’s product was found out from many tomb sites throughout Japan. It was thought that this fact suggested the ancient king’s conquest of Japan.

INTRODUCTION
The objective of this work is to develop a scientific method to determine the provenance of the Japanese ancient ceramics.

We had some kinds of ancient ceramics in Japan, such as Jomon and Yayoi pottery, and then Sueki ware. The Jomon pottery is the oldest ceramics in Japan. Yayoi pottery is a type of the ceramics produced subsequently to the Jomon pottery. On the other hand, the Sueki ware was formed by use of the potter’s
wheel, and then was baked by intense heat in excess of 1000 °C in a tunnel like kiln. This high level of technology came to Japan from the Korean peninsula in the Kofun period (about 5th century). This hardware was produced in various areas throughout Japan for the period more than seven hundreds years from 5th to 12th century. Therefore, many kiln sites have been excavated throughout Japan. From these kiln sites, potsherd has been excavated in a large quantity. Consequently, the sueki is the most useful ceramics as the material for research. For this purpose, the chemical feature of the potsherd from each kiln must be characterized at first. In this work, more than forty thousands of pieces of potsherd were analyzed by an energy dispersive X-ray fluorescence spectrometer. At the same time, neutron activation analysis of a part of these samples were carried out in the Reactor Institute of Kyoto University. As the result, the elements such as K, Ca, Rb, Sr and La were found to be useful in discriminating kilns. Japanese granitic rocks were analyzed also, to get the information on geological meanings with these elements.

Discriminant analysis was applied to determining the provenence of the earliest sueki from tomb sites.

**EXPERIMENTAL**

The potsherd was pulverized in a crucible made from tungsten carbide to the powder size below 100 mesh, after its surface was scraped off by a small grinder. The sample powder was placed in a ring made from vinyl chloride, and then was pressed under the pressure of 15 ton by a hand presser. Consequently, coin-like samples were prepared for X-ray fluorescence analysis. Their sizes were 20 mm in inner diameter and 3-5 mm in thickness. An energy dispersive X-ray fluorescence spectrometer was used. K and Ca were determined in the vaccum using Ti as a secondary target, Rb and Sr in the air using Mo target also. The peak areas as the net counts were calculated by subtracting the background areas. The JG-1 was used as the standard sample. JG-1 is the japanese granitic rock, No 1 in short. The JG-1
is the best one in the rock standard samples which are delivered from the Geological Survey of Japan, because it has the almost equal quantities of K and Ca, Rb and Sr respectively. The contents of Rb and Sr are 180 ppm and 181ppm respectively. The X-ray spectrum of JG-1 is shown in Fig. 1. Therefore, JG-1 is most useful in determining K and Ca, and then Rb and Sr at the same time. The X-ray intensities of the samples were normalized by that of JG-1. Consequently, the analytical data were expressed by the normalized values by JG-1. As an example, the calibration curve for Rb is shown in Fig. 2. Calibration curves had the good linearities between the reported values and the normalized values by JG-1 for K, Ca, Fe and Sr as well as Rb.

RESULTS AND DISCUSSION

A Rb-Sr chart was found to be best in expressing the chemical characterization of a kiln from many experimental data. Fig. 3 shows the characterization of Kokuma, Yamakuma, Yatsunami and Kougoike kilns which are located in the northern area of Kyushu island. Although there are three kilns called as Kokuma, Yamakuma and Yatsunami in Amaki city, they can not be discriminated each other, even by the other elements such as K, Ca and Fe as well as Rb and Sr. They are called the Asakura group in the lump. This result means that the same clay was used as the material in the sueki production of these kilns. The Kougoike kiln in Saga city can be easily discriminated from the Asakura group.

Fig. 4 shows the Rb-Sr chart of kilns throughout Japan. One point denotes one kiln, the average of about ten to thirty pieces of potsherid. We can recognize the general trend that the western kilns have the higher contents of Rb than the easterns, although the contents of Sr are different a little. In order to explain this result, the granitic rocks which constitute the geological basement of the Japan islands were collected and analyzed by this procedure.

At first, the granitic rocks were collected selectively from the two localities. One is from the Tsuruga peninsula as the
typical western, the other is from Mt. Hashigami as the typical eastern. These localities are shown in Fig. 5, and their Rb-Sr chart is shown in Fig. 6. It is denoted that the western granitic rocks have the higher contents of Rb, and the lower contents of Sr than the easterns. This tendency are also generally confirmed in the Rb-Sr chart of the japanese granitic rocks as shown in Fig. 7. Japanese granitic rocks are not distributed uniformly on this chart, but along the large belt, from the range of higher contents of Rb and lower contents of Sr to the reverse range. What does this distribution mean? Here, we discuss on the major elements such as K and Ca, because both Rb and Sr are the minor elements. Fig. 8 shows the correlation between K and Rb in the japanese granitic rocks. Rb has the positive co-relation with K, especially in the range less than the normalized value of about 1.0. Beyond this range, the slope of the straight is lower and the points scatter. This reason can not yet be understood. The similar relation was also obtained between Ca and Sr, as shown in Fig. 9. From these results, it can be concluded that the minor element, Rb and Sr exist with the major elements, K and Ca respectively in granitic rocks. The major minerals in granitic rocks are quartz, feldspar groups and mica. Of these minerals, only feldspar groups contain K and Ca as the important constituent elements. Especially, K exists in the potash feldspar, and on the contrary Ca is in the plagioclase also. Consequently, the result shown in Fig. 7 indicates that the granitic rocks containing potash-feldspar in much more quantities can contain plagioclase in lesser quantities only, and that the reverse is also realized. That is, the potash feldspar has the competitive relation with plagioclase in formation of granitic rocks underground.

On the other hand, sueki has the similar relation between K and Rb, Ca and Sr respectively, as shown in Fig. 10 and 11. But the Rb-Sr chart is different from that of the granitic rocks. It is caused by weathering of granitic rocks. Goldich showed that plagioclase was weathered more rapidly than potash feldspar. Therefore, the eastern clays is different a little from the wes-
tern in Ca and Sr, as shown in Fig. 4. But their difference in Ca and Sr is not marked. Baking experiments of clay to 1350 °C confirmed that its chemical characterization does not change. Next, the application to archaeology will be explained, especially on the earliest sueki.

The largest production at that time was carried out in the Sue-mura village which is located in the southern area of Osaka prefecture. Except for the Sue-mura, the earliest sueki was produced in the northern Kyushu, on the island sea side of Shikoku, in Nagoya city, central Japan and Sendai city, the southern area of Tohoku district. This author has already reported that these kilns could be discriminated each other by discriminant analysis. The Asakura’s sueki can be discriminated from the Sue-mura’s as shown in Fig. 12 where $D(o)$ and $D(1)$ are Maharanobis’ generalized distances from the Sue-mura and the Asakura, respectively. As the result that discriminant analysis was carried out in 5% dangerous probability, it was shown that the Sue-mura region was within $D^2(o)$ value of 10, the Asakura region within the $D^2(1)$ value of 10 also. Therefore, we can easily detect the Sue-mura’s sueki in the northern Kyushu by this method.

There were many tomb sites at 5-6th century in the northern Kyushu. It is generally expected that the Asakura’s sueki were provided to these tomb sites by near. But the Sue-mura’s product was found out from these tomb sites with the Asakura’ product, as shown in Fig. 13. Recently, the Sue-mura’s product was found out in many tomb sites throughout Japan. Archaeologists think that the earliest sueki was used as the religious imole-
ment and that the religious ceremony was carried out under the political authority in the ancient Japan. At that time, the japanese kings called Wao lived in Osaka, near the Sue-mura. The fact that the Sue-mura’s product was provided to many tomb sites throughout Japan should be related to the political authority of the Wao kings. That is, this fact suggests that the Wao kings conquered the ancient Japan.

Ancient Japan had the close relation with the Korean peninsula, especially with the southern area. Archaeologists say that the
korean ceramics was provided to the tomb sites in Japan. In order to solve this problem, the korean ceramics must be discriminated from the japanese sueki. Fig. 14 shows the discrimination between the korean ceramics and the Suemura’s product. K, Ca, Rb and Sr were used in calculating Maharanobis generalized distances. As separation was not complete, so K was substituted by La. Fig. 15 shows the result using Ca, Rb, Sr and La. Separation is better. This procedure will be used in future to find out the korean ceramics in the japanese tomb sites.

Fig. 1 X-ray fluorescence spectrum of JG-1

![Ti target](image1) ![Mo target](image2)

Fig. 2 Calibration curve of Rb

![Calibration curve of Rb](image3)

Regression equation \( Y = 0.0063X - 0.0888 \)

Fig. 3 Rb-Sr chart of some kilns in northern Kyushu

![Kokuma kiln](image4) ![Yamakuma kiln](image5) ![Yatsunami kiln](image6) ![Kougoike kiln](image7)
Fig. 4 Rb-Sr chart of Sueki kilns

- western kilns
- eastern kilns

Fig. 6 Rb-Sr chart of the granitic rocks of Tsuruga peninsula and Mt. Hashigami

Fig. 5 Location of Tsuruga peninsula and Mt. Hashigami

Fig. 7 Rb-Sr chart for the Japanese granitic rocks

Fig. 9 Co-relation between Ca and Sr

Fig. 8 Co-relation between K and Rb of the Japanese granitic rocks
Fig. 10 Co-relation between K and Rb for sueki kilns

Fig. 11 Co-relation between Ca and Sr for sueki kilns

Fig. 12 Discrimination of the Asakura from the Suemura’s sueki

Fig. 13 Sourcing of the sueki excavated from the tomb sites in the northern Kyushu

Fig. 14 Discrimination of the Korean Ware from the Suemura’s sueki (K, Ca, Rb, and Sr used)

Fig. 15 Discrimination of the Korean Ware from the Suemura’s sueki (Ca, Rb, Sr and La used)
REACTOR NEUTRON-INDUCED PROMPT GAMMA-RAY ANALYSIS AND
INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF DEEP SEA SEDIMENTS
IN THE PACIFIC AND THE JAPAN SEA

Yoshitaka MINAI,1 Chushiro YONEZAWA,2 Michio HOSHI,2
Yasuo ITO,3 and Takeshi TOMINAGA1

1Department of Chemistry, Faculty of Science
University of Tokyo
Hongo, Tokyo, JAPAN

2Department of Chemistry
Tokai Research Establishment, JAERI
Tokai, Ibaraki, JAPAN

3Research Center for Nuclear Science and Technology
University of Tokyo
Tokai, Ibaraki, JAPAN

ABSTRACT

Nearly 30 elements in deep sea sediments from the
Pacific and the Japan Sea were determined by reactor
neutron-induced prompt gamma-ray analysis (PGA) and
instrumental neutron activation analysis (INAA).
Element concentrations in the deep sea sediments
determined by PGA and INAA depended on sampling
locations, indicating variations in the mixing ratios
of terrigenous clastics, hydrogenous and hydrothermal
precipitates, and biogenic materials which are
regarded as source materials of marine sediments.

INTRODUCTION

The simultaneous determination of elements in geochemical
materials has been of importance to earth science. Since the
instrumental neutron activation analysis (INAA), in particular,
is useful for determination of minor and trace elements in
goechochemical materials, numerous applications of INAA to various
goechochemical substances have been reported.1) As delayed gamma-
rays from the radionuclides formed by neutron capture are
detected in INAA measurements, the sensitivity in quantitative
determination of elements can be influenced by several nuclear
parameters: cross-section for neutron capture, half-life of the
generated radionuclides, energy and relative intensity of
gamma-rays. Instead of delayed gamma-rays used in INAA, prompt
gamma-rays after neutron capture can be used for elemental and
isotopic analysis purpose.2) In this prompt gamma-ray analysis
(PGA), it is not necessary to use radionuclides with proper
half-life after neutron capture. Since cascades of gamma-rays
are usually emitted in deexcitation processes after neutron capture. It is likely that the elements without proper radionuclides formed in neutron capture may be determined by prompt gamma-ray counting. Both INAA and PGA are non-destructive multielement-analysis techniques using similar equipments including intense neutron source and gamma-ray counting system. PGA is regarded as a complementary analytical technique to INAA.

In this work we have applied PGA and INAA to determination of various elements in deep sea sediments from the Pacific Ocean and the Japan Sea. The samples includes sediments from various regions in the Pacific. Inorganic geochemistry of deep sea sediments provides a clue to elucidate sedimentation processes in various marine environments. Terrigenous clastics, hydrogenous precipitates, hydrothermal deposits, biological materials (e.g., microfossils), and organic substances compose marine sediments. The proportions of these components depend on the sedimentation environment governed by the distance from continents and hydrothermal spot in ocean bottom and biological productivity in water column. The elemental composition of sediments in the Pacific Ocean and the Japan Sea may vary with the proportions affected by the factors mentioned above.

EXPERIMENTAL

Sample description: Thirty-nine deep sea sediments collected from 19 sites (Table 1 and Fig. 1) are analyzed by INAA. Twenty samples were also analyzed by PGA. Detailed description of the samples was given previously.4)

INAA: One hundred milligrams of each pulverized sample sealed in polyethylene film with a flux monitor was irradiated with thermal neutrons (0.5 to 1.5 x 10^{12} n/cm^2/s) for 18 to 24 hours in a TRIGA-II reactor of Atomic Energy Institute, Rikkyo University. Geological reference materials issued from Geological Survey of Japan (e.g., JB-1) were also irradiated as analytical standards. After standing 7 days, gamma-rays from the samples and standards were detected with a pure Ge detector for determination of As, Br, La, Sm, and Lu. After standing 1 month, the samples were assayed again for determination of Co, Cr, Cs, Fe, Hf, Ni, Sc, Sr, Ta, Th, Zn, Ce, Eu, Tb, and Yb.

Another portion (50 mg) of each pulverized sample also sealed in polyethylene film (together with a flux monitor) was irradiated for 1 minute at a thermal neutron flux of 5 x 10^{11} n/cm^2/s in the same reactor. At 7 minutes after the end of the irradiation, the sample was assayed with a Ge(Li) detector (Atomic Energy Institute, Rikkyo University) for determination of Al, Ca, Cl, Mg, Mn, Na, Ti, and V.

PGA: One hundred milligrams of each pulverized sample sealed in fluorinated polyethylene file was irradiated with thermal neutrons (2.4 x 10^{7} n/cm^2/s) in the thermal neutron guide beam from JRR-3M reactor of Japan Atomic Energy Research Institute. Prompt gamma-rays were detected with a pure Ge detector coupled with a BGO detector for Compton suppression and pair mode counting. Most major elements and some trace
Table 1. Sampling locations. Asterisks indicate the locations where blue clay samples were collected.

<table>
<thead>
<tr>
<th>Station</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Depth (m)</th>
<th>Location in Fig. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH68-4-5</td>
<td>26°54.8N</td>
<td>169°58.6W</td>
<td>4564</td>
<td>2</td>
</tr>
<tr>
<td>KH68-4-15</td>
<td>11°39.7N</td>
<td>169°49.5W</td>
<td>5770</td>
<td>3</td>
</tr>
<tr>
<td>KH68-4-25</td>
<td>19°59.7S</td>
<td>170°03.2W</td>
<td>5280</td>
<td>4</td>
</tr>
<tr>
<td>KH68-4-29</td>
<td>26°01.7S</td>
<td>169°59.0W</td>
<td>5484</td>
<td>5</td>
</tr>
<tr>
<td>KH68-4-31</td>
<td>31°58.8S</td>
<td>169°59.7W</td>
<td>5550</td>
<td>6</td>
</tr>
<tr>
<td>KH68-4-37*</td>
<td>46°00.0S</td>
<td>169°53.0W</td>
<td>5210</td>
<td>7</td>
</tr>
<tr>
<td>KH68-4-41*</td>
<td>54°13.9S</td>
<td>169°38.0W</td>
<td>5100</td>
<td>8</td>
</tr>
<tr>
<td>KH68-4-49-3*</td>
<td>69°29.7S</td>
<td>169°58.0W</td>
<td>4200</td>
<td>9</td>
</tr>
<tr>
<td>KH69-2-23*</td>
<td>41°21.0N</td>
<td>134°26.1E</td>
<td>3575</td>
<td>19</td>
</tr>
<tr>
<td>KH70-2-7</td>
<td>33°01.9N</td>
<td>169°53.5W</td>
<td>5840</td>
<td>1</td>
</tr>
<tr>
<td>KH70-2-9</td>
<td>17°05.0N</td>
<td>146°12.3W</td>
<td>4960</td>
<td>14</td>
</tr>
<tr>
<td>KH71-1-15</td>
<td>12°03.6N</td>
<td>130°10.8E</td>
<td>5700</td>
<td>10</td>
</tr>
<tr>
<td>KH71-5-53</td>
<td>8°15.3N</td>
<td>112°42.1W</td>
<td>3970</td>
<td>15</td>
</tr>
<tr>
<td>KH73-4-4</td>
<td>12°37.8N</td>
<td>151°30.5E</td>
<td>5920</td>
<td>11</td>
</tr>
<tr>
<td>KH73-4-6</td>
<td>10°45.9N</td>
<td>153°42.0E</td>
<td>5700</td>
<td>12</td>
</tr>
<tr>
<td>KH73-4-9</td>
<td>7°59.9S</td>
<td>172°48.6E</td>
<td>5390</td>
<td>13</td>
</tr>
<tr>
<td>KH77-1-6*</td>
<td>39°41.4N</td>
<td>145°22.2E</td>
<td>5325</td>
<td>16</td>
</tr>
<tr>
<td>KH77-1-7*</td>
<td>39°49.5N</td>
<td>144°04.0E</td>
<td>5270</td>
<td>17</td>
</tr>
<tr>
<td>KH77-1-8*</td>
<td>40°39.7N</td>
<td>143°19.0E</td>
<td>1650</td>
<td>18</td>
</tr>
</tbody>
</table>

elements (e.g., B) were determined in the Compton suppression mode spectra. Details of the PGA system and analytical procedures were reported in literature.5,6)

RESULTS AND DISCUSSION

The analytical results are summarized in Tables 2 and 3. Whenever an element could be determined by both INAA and PGA, the INAA result was preferred because more samples were analyzed. Since concentrations of lanthanides were reported previously, they are omitted in Tables 2 and 3.

Sediment samples can be classified into red clay (pelagic sediment) and blue clay (Table 1); these two types of sediments and calcareous and siliceous biogenic elements represent the marine sediments covering most areas of ocean bottom. Some transition elements (Mn, Co, Ni, and Zn) tended to occur in higher concentrations in the red clay samples (Tables 2 and 3). While red clay covers ocean plain with lower sedimentation rate, blue clay is found in continental slope and polar area with high sedimentation rates because of high influx rates of terrigenous materials. Manganese has been regarded as a typical hydrogenous elements, and dilution of hydrogenous components by terrigenous materials may lead to lower manganese concentrations in the blue clay samples. The other transition elements abundant in the red clay samples may be associated
with manganese in hydrogenous precipitation.

In Fig. 2 is plotted the MnO content against the Al₂O₃ content in the sediment samples. The Al content was conversely correlated to the Mn content in both types of sediments. The relationship between the Al and Mn contents suggests different source materials for Al and Mn. As noted above, hydrogenous deposition is regarded as a major transport process of manganese into oceanic sediments. Terrigenous clastics like kaolinite may supply aluminum to the sediments. It may be worthwhile to note that the correlation between Al₂O₃ and Mn contents was slightly different for the red clay and the blue clay samples: such a discrepancy may reflect transport of manganese during diageneis of blue clay samples. Similar results were also obtained with the Co, Ni, and Zn concentrations, suggesting that these elements are also like manganese.

The aluminum-manganese plot (Fig. 2) suggests large difference in mixing ratios of terrigenous and hydrogenous components in the sediment samples. The elemental concentrations in the sediments can be expected as a measure for regional variations of these components. However, direct plots of the elemental concentrations themselves on the location map did not simply indicate any systematic regional variation of mixing ratio of terrigenous and hydrogenous components, such as Al and Mn contents probably because biogenic materials were also supplied to the sediments. Even if contents of the elements were very low in the biogenic materials, the concentrations in the sediments should be influenced according to dilution by the biogenics. Plots of elemental concentration ratios, for example, can represent regional variation in those components free from dilution and other effects by sedimentation of biogenic materials; shale-normalized REE (rare earth element) pattern is regarded as one of such parameters. As reported previously, the patterns of the sediments depended on the sampling locations, indicating systematic variations in the mixing ratio of terrigenous and hydrogenous components in the Pacific.

Figure 3A represent latitudinal variations of La/Yb,
Table 2. Contents of major elements in the sediment samples. Asterisks indicate blue clay samples.

<table>
<thead>
<tr>
<th>Station, Depth (cm)</th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>TiO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>MnO (%)</th>
<th>MgO (%)</th>
<th>CaO (%)</th>
<th>Na₂O (%)</th>
<th>K₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH68-4-5,50</td>
<td>46.5</td>
<td>15</td>
<td>0.8</td>
<td>8.0</td>
<td>0.36</td>
<td>0.8</td>
<td>2.5</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>KH68-4-5,100</td>
<td>46.5</td>
<td>13</td>
<td>0.3</td>
<td>6.4</td>
<td>0.71</td>
<td>3.7</td>
<td>1.1</td>
<td>4.4</td>
<td>3.0</td>
</tr>
<tr>
<td>KH68-4-15,50</td>
<td>46.5</td>
<td>13</td>
<td>0.5</td>
<td>6.2</td>
<td>0.9</td>
<td>4.0</td>
<td>3.5</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>KH68-4-15,100</td>
<td>44.5</td>
<td>12</td>
<td>0.1</td>
<td>8.8</td>
<td>0.5</td>
<td>4.5</td>
<td>3.3</td>
<td>3.3</td>
<td>2.4</td>
</tr>
<tr>
<td>KH68-4-25,50</td>
<td>44.5</td>
<td>12</td>
<td>0.6</td>
<td>8.3</td>
<td>0.67</td>
<td>4.3</td>
<td>2.2</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>KH68-4-25,100</td>
<td>50.7</td>
<td>12</td>
<td></td>
<td>7.5</td>
<td>0.67</td>
<td>2.9</td>
<td>3.5</td>
<td>3.2</td>
<td>2.4</td>
</tr>
<tr>
<td>KH68-4-29,50</td>
<td>50.7</td>
<td>13</td>
<td>0.9</td>
<td>8.1</td>
<td>0.66</td>
<td>4.7</td>
<td>3.5</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>KH68-4-29,100</td>
<td>47.0</td>
<td>13</td>
<td>0.5</td>
<td>6.8</td>
<td>0.51</td>
<td>4.6</td>
<td>2.2</td>
<td>4.1</td>
<td>2.4</td>
</tr>
<tr>
<td>KH68-4-31,50</td>
<td>47.0</td>
<td>14</td>
<td>0.2</td>
<td>3.6</td>
<td>0.35</td>
<td>2.7</td>
<td>1.9</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>KH68-4-31,100</td>
<td>54.8</td>
<td>17</td>
<td>0.8</td>
<td>6.5</td>
<td>0.1</td>
<td>5.7</td>
<td>2.8</td>
<td>4.1</td>
<td>3.9</td>
</tr>
<tr>
<td>KH68-4-37,50*</td>
<td>62.1</td>
<td>16</td>
<td>0.7</td>
<td>6.5</td>
<td>0.1</td>
<td>5.7</td>
<td>2.8</td>
<td>4.4</td>
<td>3.9</td>
</tr>
<tr>
<td>KH68-4-37,100*</td>
<td>44.2</td>
<td>9.9</td>
<td>0.6</td>
<td>5.5</td>
<td>0.35</td>
<td>1.4</td>
<td>3.8</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>KH68-4-41,100*</td>
<td>11</td>
<td>0.8</td>
<td>5.6</td>
<td>0.25</td>
<td>1.6</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH68-4-49,3,50*</td>
<td>41.2</td>
<td>13</td>
<td>1.0</td>
<td>6.6</td>
<td>0.2</td>
<td>0.9</td>
<td>2.9</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>KH68-4-49,3,100*</td>
<td>59.9</td>
<td>14</td>
<td>0.6</td>
<td>7.1</td>
<td>0.09</td>
<td>1.3</td>
<td>3.2</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>KH70-2-7,50</td>
<td>48.4</td>
<td>16</td>
<td>0.8</td>
<td>6.7</td>
<td>0.11</td>
<td>1.4</td>
<td>2.0</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>KH70-2-7,100</td>
<td>14</td>
<td>0.9</td>
<td>6.5</td>
<td>0.53</td>
<td>1.1</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH70-2-9,50</td>
<td>44.4</td>
<td>10</td>
<td>0.3</td>
<td>6.0</td>
<td>0.94</td>
<td>0.8</td>
<td>2.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>KH70-2-9,100</td>
<td>49.8</td>
<td>11</td>
<td>0.6</td>
<td>5.7</td>
<td>0.88</td>
<td>0.7</td>
<td>2.8</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>KH71-1-15,50</td>
<td>48.6</td>
<td>14</td>
<td>0.6</td>
<td>8.2</td>
<td>0.86</td>
<td>1.3</td>
<td>3.0</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>KH71-1-15,100</td>
<td>14</td>
<td>0.7</td>
<td>8.4</td>
<td>0.74</td>
<td>0.8</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH71-5-58,100</td>
<td>28.4</td>
<td>5.3</td>
<td>0.5</td>
<td>11</td>
<td>1.3</td>
<td>3.7</td>
<td>2.7</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>KH73-4-4,50</td>
<td>13</td>
<td>0.7</td>
<td>8.3</td>
<td>0.79</td>
<td>2.0</td>
<td>1.0</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH73-4-4,100</td>
<td>44.4</td>
<td>13</td>
<td>0.4</td>
<td>8.2</td>
<td>0.87</td>
<td>1.5</td>
<td>3.7</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>KH73-4-6,30</td>
<td>40.3</td>
<td>12</td>
<td>0.9</td>
<td>7.7</td>
<td>0.64</td>
<td>2.1</td>
<td>4.4</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>KH73-4-9,30</td>
<td>12</td>
<td>0.2</td>
<td>9.3</td>
<td>0.84</td>
<td>4.8</td>
<td>3.7</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH73-4-9,100</td>
<td>32.9</td>
<td>11</td>
<td>1.0</td>
<td>9.6</td>
<td>0.98</td>
<td>5.2</td>
<td>3.7</td>
<td>3.5</td>
<td>2.4</td>
</tr>
<tr>
<td>KH77-1-6,2*</td>
<td>48.8</td>
<td>12</td>
<td>0.5</td>
<td>3.7</td>
<td></td>
<td>1.3</td>
<td>6.1</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>KH77-1-7,50*</td>
<td>66.4</td>
<td>8.0</td>
<td>0.5</td>
<td>3.2</td>
<td>0.04</td>
<td>2.9</td>
<td>0.9</td>
<td>4.4</td>
<td>3.7</td>
</tr>
<tr>
<td>KH77-1-7,100*</td>
<td>8.0</td>
<td>0.4</td>
<td>3.4</td>
<td>0.03</td>
<td>2.1</td>
<td>1.9</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH77-1-8,50*</td>
<td>13</td>
<td>0.2</td>
<td>6.6</td>
<td>0.08</td>
<td>3.8</td>
<td>4.2</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH77-1-8,100*</td>
<td>13</td>
<td>0.6</td>
<td>5.7</td>
<td>0.08</td>
<td>3.5</td>
<td>3.0</td>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,86*</td>
<td>14</td>
<td>0.8</td>
<td>5.0</td>
<td>0.08</td>
<td>0.6</td>
<td>3.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,150*</td>
<td>14</td>
<td>0.6</td>
<td>5.0</td>
<td>0.11</td>
<td>0.7</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,210*</td>
<td>14</td>
<td>0.9</td>
<td>5.6</td>
<td>0.06</td>
<td>2.0</td>
<td>3.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,270*</td>
<td>14</td>
<td>0.5</td>
<td>4.6</td>
<td>0.23</td>
<td>2.5</td>
<td>3.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,830*</td>
<td>15</td>
<td>0.6</td>
<td>5.6</td>
<td>0.11</td>
<td>1.9</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KH69-2-23,936*</td>
<td>15</td>
<td>0.7</td>
<td>5.8</td>
<td>0.11</td>
<td>1.0</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ce/Ce*, and Eu/Eu* ratios (Ce* and Eu*: Ce and Eu concentrations estimated from interpolation of La, Sm, and Tb concentrations on REE pattern) in the sediments from sampling sites along 170°W. These ratios were applied successfully to elucidate history of sedimentation in the regions adjacent to the Japanese Islands. 9,10 It is remarkable that the Ce/Ce* ratios in the sediments from the equatorial areas were below 1,

Fig. 2. Correlation between $\text{Al}_2\text{O}_3$ and MnO contents. Closed circles: red clay. Open circles: blue-clay from the South Pacific. Open triangles: blue clay from the Japan Trench. Open squares: blue clay from the Japan Sea.

Fig. 3. The La/Yb, Eu/Eu$^*$, and Ce/Ce$^*$ ratios of the deep sea sediments collected along the 170$^\circ$W (a) and in the equatorial area (b).
materials was lower in the equatorial area of the middle-to-eastern Pacific than in the western Pacific. The La/Yb ratio remained nearly constant in the sediments from the equatorial region (Fig. 3(B)) whereas the ratio depended on the latitude of the sampling locations as mentioned (Fig. 3(A)). The variations of these ratios were not identical to those of Ce/Ce* ratio, which may be an indicator of mixing ratio of hydrogenous materials. It was reported that the REE patterns of the Japan Sea sediments were different from those of the Japan Trench sediments whereas the patterns of the both sediments did not indicate any Ce depletion (Ce/Ce*<1).”7

Perhaps, La/Yb ratios in the Pacific sediments are dependent on the ratios in the terrigenous source materials.

We have demonstrated in this paper that analytical techniques based on neutron activation are quite helpful in geochemical studies of oceanic sediments. Nearly 30 elements in oceanic sediments can be determined by INAA and PGA without sample decomposition. The elemental ratios and the parameters calculated from the elemental compositions provides clues to elucidate sedimentation processes in marine environment. It is also noteworthy that the samples once analyzed can be further used for duplicate analysis or analysis by other methods, if necessary. Oceanic sediments are composed of various minerals, organics, and biogenics. Such heterogeneity of sediment samples sometimes introduces unexpected discrepancy in analytical results and requires duplicate analysis and cross-checking of the obtained concentrations. Based on INAA and PGA, we can avoid to some extent, such problems encountered in analysis of heterogenous samples.

REFERENCES

REACTOR NEUTRON-INDUCED PROMPT GAMMA-RAY ANALYSIS AND INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF ANCIENT GLASSWARE

T. TOMIZAWA\textsuperscript{1}, C. YONEZAWA\textsuperscript{2}, Y. MINAI\textsuperscript{3}, H. HOSHI\textsuperscript{2}, Y. ITÔ\textsuperscript{4} and T. TOMINAGA\textsuperscript{3}

1) Faculty of Literature, Keio University, Mita, Tokyo, Japan
2) Japan Atomic Energy Research Institute
3) School of Science, University of Tokyo, Hongo, Tokyo, Japan
4) Research Center for Nuclear Science and Technology, University of Tokyo, Yayoi, Tokyo, Japan

ABSTRACT

Elemental composition of ancient glassware provides a clue to estimate provenance, source material, and manufacturing procedures. In determination of their compositions it is usually desirable to apply non-destructive analytical techniques because even the shape of artifacts should be preserved as excavated for future studies. Reactor neutron-induced prompt gamma-ray analysis (PGA), instrumental neutron activation analysis (INAA), and X-ray fluorescence analysis (XRF) are simultaneous multielement analytical methods providing information on elemental composition. Beside, both techniques are non-destructive method, which are appropriate for studies of such artifacts. In this work we have reported the elemental composition of ancient glassware (from the Yayoi period to the Edo period) excavated from the ruins in Japan to estimate provenance, source material, and manufacturing procedures.
Neutron beam from JRR-3M at JAERI was employed for reactor neutron-induced PGA. Fluctuation in neutron flux were monitored by a neutron counter and duplicate PGA measurements of a titanium foil. Triga II reactor at Rikkyo University was used for conventional INAA. Some standard reference materials were employed as analytical standard for quantitative analysis purpose.

Concentrations of several elements (e.g., chlorine) determined by PGA were compared with the concentrations obtained by INAA. The analytical results obtained by either method were in good agreement with each other if the analytical precisions were given in terms of counting statistics of the corresponding photo peak.

Elemental composition of the ancient glassware determined by PGA and INAA varied largely with the age of manufacturing and the location of the ruin, indicating history and provenance of the source materials used for manufacturing of the glassware. Some elements were expected to be added on purpose to color the glassware of the basis of the determinations.

1. Introduction
Reactor neutron-induced prompt gamma-ray analysis (PGA), instrumental neutron activation analysis (INAA), and X-ray fluorescence analysis (XRF) are rapid non-destructive simultaneous multielement analytical methods on elemental composition of archaeological artifacts. These methods have been applied to determine the major and trace elements of glassware.

2. Experimental procedures
2.1 X-ray fluorescence analysis
A 100 mCi $^{241}$Am source was employed to induce fluorescence X-rays from the glass samples. The fluorescence X-rays were detected and analyzed by means of a Si(Li) X-ray detector coupled with a 2048 channel pulse height analyzer. The typical measuring time was 3000 seconds.
2.2 Neutron activation analysis

About 30 mg of samples were weighed into polyethylene set sealed before irradiation. Capsules containing of such samples were irradiated in the Triga II reactor at the nuclear research institute of Rikkyo University for 3 minutes (thermal neutron flux: \(1.5 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}\)) and 18 hours (thermal neutron flux: \(1.5 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}\)).

The gamma-ray detection system used in this study consisted of 50 cm² lithium drifted germanium detector coupled to a 4096 channel pulse height analyzer. After neutron irradiation the samples and standard were made three measurements. The short lived radioactive species were measured for 5 minutes after a cooling period of 5 minutes to allow the \(^{28}\text{Al}\) activity to decay. The second counting of sample was made after a cooling period of 1 week for 3000 seconds and 4 weeks later for 20000 seconds.

After the counting all peak areas were corrected for decay and counting losses and compared with those obtained from weighed samples and standards. All samples and standards were irradiated and measured in the similar manner.

2.3 Reactor neutron-induced prompt gamma-ray analysis

Neutron beam from JRR-3M at JAERI was used for reactor neutron-induced PGA. Fluctuation in neutron flux were monitored by a neutron counter and duplicate PGA measurements of a titanium foil.

Samples were sealed into fluorinated ethylenepropylene resin film (FEP, 25 \(\mu\)m in thickness). The samples were set on the sample chamber from which the air was purged with the flow of He gas. The sample chamber was made of polytetrafluoroethylene (PTFE, Teflon). The gamma-ray spectrometer consists of a high purity Ge detector, and BGO (bisumuth germanate, \(\text{Bi}_4\text{Ge}_3\text{O}_{12}\) ) shielding detector coupled with a 8192 channel pulse height analyzer.

In measurements we have used the following spectrometer system, which can measure simultaneously the prompt gamma-ray energy (0 - 12 MeV). A single mode, a Compton suppression mode, and a pair mode were performed. The thermal neutron flux was determined to be \(2.4 \times 10^7 \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}\) and the cold neutron flux was found to be \(1.1 \times 10^8 \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}\). The
samples were measured for about 3000 seconds for the cold neutron beam.

3. Results and discussions

Glass is one of the oldest man-made materials and the most important artifacts in the world. The prehistoric period of Japan is divided into the Jomon period (before ca. 300 B.C.) and the Yayoi period (ca. 300 B.C.-ca. 300 A.D.). No glass has been found in the Jomon period. In the Yayoi period, glassware has been found in several sites. In Kofun period (Tumulus period, from ca. third century A.D. to the seventh century), glass beads have been excavated in several tombs. In that period, most of the glass beads were made of mixed-alkali glass.

Glass are obtained by the fusion of silica and some metal oxides. They are mixtures of the following components: silica (SiO₂), alumina (Al₂O₃), lime (CaO), magnesia (MgO), soda (Na₂O), potash (K₂O), manganese oxide (MnO), ferric oxide (Fe₂O₃), tin oxide (TiO₂), and lead oxide (PbO). The proportions of soda and potash (alkali oxide) vary widely. Table 1 lists some of the most common metal ions used by ancient glass makers to color glass. The color of glass is determined by the presence of various metallic oxides, usually in small amounts. Iron is the almost universal coloring agent of ancient glasses. Iron is usually present in glass as a mixture of ferrous ions (Fe²⁺), which color the glass blue. And ferric ions (Fe³⁺) gives it yellow. Many ancient glasses were colored by the presence of oxidized cobalt and copper; cobalt ions (Co²⁺) give glass dark blue color and cupric ions (Cu²⁺) bright blue color.

About two thousand samples of ancient Japanese glass were analyzed X-ray fluorescence analysis². The results revealed the existence of four compositional groups as shown in Table 2. The lead-barium glass beads are known to have been made in ancient China (Pre-Han and Han dynasty (202 B.C. -220 A.D.))³⁴. In Figure 1 a typical X-ray fluorescence spectrum of lead-alkali glass bead is shown: the Cu X-ray Kα line, Ba Kα lines, Sn Kα line, Fe Kα line, Mn Kα line, and Pb L lines can be seen.

Neutron activation analysis was applied to the glass beads
of the Edo period. Results of the analysis of the major and trace components are presented in Table 3. Glass beads are of lead glass type, except for the blue bead, which is of soda-lime type.

A typical prompt gamma-ray spectrum of glass beads (potash-lime glass bead, the Edo period, excavated at the Kaneiji Temple in Tokyo) is shown in Figure 2. Elements such as boron, sodium, potassium, chlorine, and silicon can be measured in high sensitivity at the thermal neutron beam. The content of boron indicates of the difference in raw materials for manufacturing glass. Boron content was in the 20 - 80 ppm range.

A plot of K2O (Wt%) vs Na2O (Wt%) indicates that there may indeed be three compositional type. The groups can be characterized according to the concentration of three oxides: lead (PbO), sodium (Na2O) and potassium (K2O). Variation in the concentrations of soda and potash are probably due to the compositional variation of the raw materials used in manufacture.

4. Conclusions

PGA, INAA and XRF can be successfully applied to ancient glass beads because of their ability of rapid non-destructive simultaneous multielement analyses. The methods have been found to be applicable to archaeological samples in general. Because of these advantages it may be applicable to other precious objects of cultural property. The analysis of samples provides a clue to estimate provenance, raw materials, and manufacturing procedures. Based on the contents of boron, sodium, potassium, chlorine, silicon, barium, and lead, ancient Japanese glass beads could be characterized.

REFERENCES
Table 1  Glass-coloring ions

<table>
<thead>
<tr>
<th>Color of glass</th>
<th>Metal ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue</td>
<td>Cupric(Cu²⁺)</td>
</tr>
<tr>
<td></td>
<td>Cobalt(Co²⁺)</td>
</tr>
<tr>
<td>Green</td>
<td>Cupric(Cu²⁺)</td>
</tr>
<tr>
<td></td>
<td>Ferrous(Fe²⁺)</td>
</tr>
<tr>
<td>Amber</td>
<td>Ferric(Fe³⁺)</td>
</tr>
<tr>
<td>Yellow</td>
<td>Uranium(U⁴⁺)</td>
</tr>
<tr>
<td>Red</td>
<td>Cuprous(Cu²⁺)</td>
</tr>
<tr>
<td>Violet</td>
<td>Manganous(Mn²⁺)</td>
</tr>
</tbody>
</table>

Table 2  Chemical composition of Japanese glass beads

<table>
<thead>
<tr>
<th>Period</th>
<th>Cobalt blue</th>
<th>Blue</th>
<th>Green</th>
<th>Yellow</th>
<th>Brown</th>
<th>White</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yayoi period</td>
<td>Soda-potash-lime</td>
<td>Soda-potash-lime</td>
<td>Soda-potash-lime</td>
<td>Lead glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3C-3C-3C)</td>
<td>glass</td>
<td>glass</td>
<td>glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium-potash</td>
<td>Sodium-potash</td>
<td>Sodium-potash</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>silicate</td>
<td>silicate</td>
<td>silicate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>glass</td>
<td>glass</td>
<td>glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodium-potash</td>
<td>Sodium-potash</td>
<td>Sodium-potash</td>
<td>Lead glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>silicate glass</td>
<td>silicate glass</td>
<td>silicate glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>glass</td>
<td>glass</td>
<td>glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nara period</td>
<td>Lead glass</td>
<td>Lead glass</td>
<td>Lead glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4C-7C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heian period</td>
<td></td>
<td>Lead glass</td>
<td>Lead glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(794-1191)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eda period</td>
<td></td>
<td>Lead glass</td>
<td>Lead glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1607-1873)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1  X-ray fluorescence spectrum

Figure 2  Prompt gamma-ray spectrum
Table 3 Analyses of Japanese glass beads

<table>
<thead>
<tr>
<th>Colour</th>
<th>White</th>
<th>Brown</th>
<th>Green</th>
<th>Blue</th>
<th>Potash-Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lead glass</td>
<td>Lead glass</td>
<td>Lead glass</td>
<td>Lead glass</td>
<td></td>
</tr>
<tr>
<td>Weight</td>
<td>60.0(mg)</td>
<td>35.4(mg)</td>
<td>37.2(mg)</td>
<td>50.0(mg)</td>
<td>43.9(mg)</td>
</tr>
<tr>
<td>Al₂O₃(%)</td>
<td>1.03</td>
<td>0.34</td>
<td>0.88</td>
<td>1.51</td>
<td>2.71</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.16</td>
<td>0.14</td>
<td>0.15</td>
<td>0.27</td>
<td>3.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.9</td>
<td>0.3</td>
<td>8.0</td>
<td>8.8</td>
<td>13.4</td>
</tr>
<tr>
<td>CaO</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>9.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.14</td>
</tr>
<tr>
<td>MgO</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.29</td>
<td>n.d.</td>
</tr>
<tr>
<td>MnO</td>
<td>0.005</td>
<td>0.001</td>
<td>0.19</td>
<td>0.24</td>
<td>0.005</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.13</td>
<td>3.78</td>
<td>0.19</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>Sc(ppm)</td>
<td>1.3</td>
<td>2.0</td>
<td>2.7</td>
<td>1.5</td>
<td>0.60</td>
</tr>
<tr>
<td>V</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>10</td>
<td>7.8</td>
</tr>
<tr>
<td>Cr</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>51</td>
<td>n.d.</td>
</tr>
<tr>
<td>Co</td>
<td>9.1</td>
<td>0.10</td>
<td>1.2</td>
<td>390</td>
<td>3.9</td>
</tr>
<tr>
<td>Cu</td>
<td>190</td>
<td>430</td>
<td>9500</td>
<td>630</td>
<td>6500</td>
</tr>
<tr>
<td>As</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>17</td>
</tr>
<tr>
<td>Ag</td>
<td>89</td>
<td>210</td>
<td>19</td>
<td>150</td>
<td>3.3</td>
</tr>
<tr>
<td>Rb</td>
<td>35</td>
<td>47</td>
<td>43</td>
<td>120</td>
<td>n.d.</td>
</tr>
<tr>
<td>Sb</td>
<td>500</td>
<td>140</td>
<td>220</td>
<td>3200</td>
<td>15</td>
</tr>
<tr>
<td>La</td>
<td>0.14</td>
<td>0.72</td>
<td>0.24</td>
<td>1.3</td>
<td>7.0</td>
</tr>
<tr>
<td>Ce</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>82</td>
<td>19</td>
</tr>
<tr>
<td>Sm</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.07</td>
<td>n.d.</td>
<td>0.13</td>
</tr>
<tr>
<td>Eu</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.25</td>
</tr>
<tr>
<td>Tb</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.11</td>
</tr>
<tr>
<td>Yb</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.15</td>
<td>0.87</td>
<td>n.d.</td>
</tr>
<tr>
<td>Lu</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.38</td>
<td>n.d.</td>
</tr>
<tr>
<td>Hf</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.87</td>
<td>0.87</td>
</tr>
<tr>
<td>Th</td>
<td>2.8</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.3</td>
<td>4.9</td>
</tr>
</tbody>
</table>
APPLICATION OF NEUTRON RADIGRAPHY TO PLANT RESEARCH AND WATER HYDROLOGY IN SOIL

Tomoko M. Nakanishi, Satoshi Matsumoto, Hisako Matsumoto, Akiko Yasunishi, Hisao Kobayashi, Akira Tsuruno

Faculty of Agriculture, Univ. of Tokyo, 1-1-1, Yayoi, Bunkyo-ku, Tokyo, 113 Japan

Institute for Atomic Energy, Rikkyo Univ., 2-5-1, Nagasaka, Yokosuka-shi, Kanagawa-ken, Japan

Department of Research Reactor, Japan Atomic Energy Institute, 2-4, shirane Shirakata Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

Neutron radiography (NR) has been mainly applied in engineering and industrial field. The authors tried to apply NR to plant research to investigate the morphological pattern of the root in the soil as well as the water movement near the root, for the first time in Japan. The authors grew soybean in a thin aluminum container and the sample was irradiated with thermal neutron, periodically, while the growth of the plant. For the morphological change of the root, until the first and the second root development were clearly shown by NR. In the case of water movement near the root, the movement was more clearly shown when the standard sand was used. Since the darkness of the soil correlates well to the deficiency of the soil, image analysis was performed to know the water movement near the root. The gradient of the water content near the root was steeper at the upper half of the root. When water absorbing polymers (polyacrylic polymer and polyvinyl alcohol copolymer), which have been expected to improve the desert for their water sustaining ability, were added to compare the water movement near the root.

INTRODUCTION

Soil deterioration is now a world wide problem. For example, turning the desert to the green land has been tried in various ways. However the experiment to know the actual water movement in soil has been hardly reported, though, which is the most essential factor to find the way to recover the desert to grow the plants or to clarify the mechanism of growing desert. One of the reason is that the actual experiment to know the water kinetics is difficult to perform. Therefore, various theoretical approaches have been carried out, based on so called micro- and macro models. These models have many problems, especially, in dealing with the plant root, therefore, the cal-
culations tended to be different from the actual water movement in soil.

In this research, neutron radiography (NR) was introduced for the first time in this field to investigate the actual water kinetics around the developing root, directly and non-destructively. The evaluation of the water absorbing polymers, which have been gathering the attention to improve the desert land, was also performed. For the evaluation, the NR image was analyzed by computer to know the actual water movement in the soil.

EXPERIMENTAL

Seed of soybean (Glycine Max L. Merril. c.v. Kitamusume) was washed with 1% hypochlorite solution and was germinated at 25°C. When the root length became about 5cm, the plant was put on the top of the aluminum container where the sand or the sand containing water absorbing polymer with 18% of water was packed. The sand used was Toyoura test sand which mesh size was between 105-297μm. Two types of water absorbing polymers were used, polyacrylic polymer (PA, Acryhope, Nippon Shokubai Kagaku Kogyo Co.) and polyvinyl alcohol copolymer (PVA, Mizumachi-ichiban, Nippon Gosei Kagaku Kogyo Co.). Both polymers were supplied in powder form and the polymer particles, which mesh sizes were between 1mm and 1.5mm were selected. The polymers were first swelled well and then added to the sand to be 0.3% in dry weight, and mixed well. The plants growing in the aluminum containers were grown in a phytotron at 25°C with sufficient light of 20,000 lx. Then after 5, 6, 10 and 12 days the plants were taken out from the phytotron and exposed to the thermal neutron at Rikkyo TRIGA-II reactor.

To get the NR image, the plant with the container was fixed on a cassette where neutron converter (Sakura K5050) and dry film (Sumitomo 3M dry film) were sealed in a vacuum. The cassette with the sample was set vertically and the total thermal neutron flux was 8.7×10⁶n/cm².

RESULTS AND DISCUSSION

Figure 1 shows the soybean seedling grown for 5, 6, 10 and 12 days in the aluminum container (150mm×70mm×50mm) packed with Toyoura test sand. Whiter part in the image means that the water content is higher than the darker part. Since plant root contains more water than the sand, the root pattern was clearly indicated in the picture. The darker part is a water deficient part. The water amount and the darkness correlated well as we reported(1). The darker part around the main root indicates that at this point the water uptake by the plant is higher than the rest part of the root.

Figure 2 shows the soybean seedling growing in the sand containing polyacrylic(PA) polymer for the same period and in the same size of the container as Fig. 1. As is shown in the figure, the root development was not well compared to that in the sand alone (Fig. 1). Not only the main root but also the side root did not develop well and the length of the main root remained about the same size throughout the period examined. The white spots in the sand indicate the polymer. The contrast of the polymer image becomes more distinguished as the day proceeds, which means that the darkness, i.e. water deficiency, of the sand proceeds. From 5 to 12 days, the polymer size did not change while the deficiency of water in the sand proceeded. The un-
changed size and color tone of any polymer in the image indicated that the water absorbed in the polymer was not supplied to the plant.

Figure 3 shows the soybean root grown for the same period and in the same size of the container as Fig. 1, where the sand and polyvinyl alcohol (PVA) copolymer was added. The root development was much better than that when PA polymer was added (Fig. 2). Both main and side roots developed as well as those in the sand alone (Fig. 1). At the upper part of the root the color tone of the sand became darker, similar to Fig. 1 and Fig. 2. However in Fig. 3, the size of the polymers, especially connecting to the upper side roots comes to be smaller at 10 and 12 day old sample. This phenomenon indicated that at first, the water was supplied from the sand and then water was supplied from the polymers. Some of the polymers around the main root were completely disappeared on 12 day old sample.

Figures 4 to 12 shows the water content in the soil measured by image analysis of NR picture, corresponding to 10 day old image of Fig. 1, 2 and 3. Figures 4, 7, 10. Figures 5, 8, 11 and Figures 6, 9, 12 are the analysis of Figure 1, 2 and 3, respectively. Figures 4, 5 and 6 are the water content of the soil adjacent to the right side of the main root, less than 1mm in distance, corresponding to Figures 1, 2 and 3, respectively. Figures 7, 8 and 9 are the water content in the soil measured at 0, 0.5, 1.0 and 1.5cm far from the right side of the main root in Figures 1, 2 and 3, respectively. Figures 10, 11 and 12 are the three dimensional expression of Figures 7, 8 and 9, respectively. The vertical line in Figures 4 to 12 indicates the degree of the darkness in the picture, i.e. relative water content in the soil. The horizontal line in Figures 4 to 12 are the depth of the measuring point from the surface of the soil. The crossing line formed by horizontal and vertical plane in Figures 10 to 12 indicates where the root is.

Figures 4 and 5 indicate that the water was absorbed at relatively upper part of the root and there was the minimum part in water deficiency near the root. However in Fig. 5 no such tendency is observed, suggesting either the water movement in the soil was small or root development was not in good condition.

When the water content around the root was measured till 1.5cm far from the root, the gradient of the water flow toward the root was measured, as indicated in Figures 7 to 9. In these cases, the water around the root which depth was from 2 to 6cm from the surface of the soil was investigated. The darkest column in Figures 7 to 9 shows the water content closest to the root. When the difference between the darkest column and the column with cross, which is the right side one, is larger, the water gradient at that root point is greater. The greater gradient was shown in Fig. 7 than 8 or 9, indicating that water was supplied first from the soil and not from the polymers. Therefore, when the water absorbing polymer exists, first, the water in the soil which is relatively far from the main root was supplied, resulting relatively flat water movement shown in Figures 11 or 12.

To determine the water content accurately, various factors for the calibration of the image, such as to correct the inhomogeneous neutron flux in the irradiating field, have to be estimated.

The neutron radiography was shown to be a useful method in plant research, especially, for the method made it possible to analyze the condition of the plant and soil system during the growth of the plant, non-destructively. The application field of neutron radiography in plant research is expected to become wider as the data using plants are accumulated.
Fig. 1 NR image of soybean seedling grown for 5, 6, 10 and 12 days in the aluminum container packed with Toyoura test sand.

Fig. 2 NR image of soybean seedling grown for the same period as Fig. 1 in the same size of the aluminum container packed with sand containing polyacrylic water absorbing polymer.

Fig. 3 NR image of soybean seedling for the same period as Fig. 1 and Fig. 2 in the same aluminum container packed with sand containing polyvinyl alcohol copolymer.
Fig. 4 Water content in soil at the root of Fig. 1, 10 days

Fig. 5 Water content in soil at the root of Fig. 2, 10 days, with PA polymer

Fig. 6 Water content in soil at the root of Fig. 3, 10 days, with PVA polymer
Fig. 7 Water content in soil
(corresponds to Fig. 1, 10 days)

Fig. 8 Water content in soil with PA polymer
(corresponds to Fig. 2, 10 days)

Fig. 9 Water content in soil with PVA polymer
(corresponds to Fig. 3, 10 days)
Fig. 10 Three dimensional water content in soil (corresponds to Fig. 1, 10 days)

Fig. 11 Three dimensional water content in soil with PA polymer, corresponds to Fig. 2, 10 days

Fig. 12 Three dimensional water content in soil with PVA polymer, corresponds to Fig. 3, 10 days
THE CADMIUM CONTENT IN BONE OF OSTEOPOROTIC PATIENTS

M. TERAI, K. IIZUKA and *M. EGUCHI
Department of Life Environment, School of Social Information Study
OTSUMA WOMEN'S UNIVERSITY
Tama, Tokyo 206, Japan.

*Department of Anatomy, Kanto Rosai Hospital
Nakahara-ku, Kawasaki 211, Japan

Abstract

There are about 50 elements in the human body. A half of them is the essential elements in the organism. The residual elements except main constituents are called the essential trace elements for the organism. Trace elements in human body are very important for physical reactions of life. There is an osteoporosis that is one of the old person's disease. The osteoporosis happened by changing some physical nature of bone with aging. Or hormone imbalance and deficiency of calcium intake degenerated the bone in quality, too. The trace elements in human organ tissues and human bone tissues were determined to make clear distribution of trace elements in the human body by neutron activation analysis. Very much cadmium was found in human bones of osteoporotic patients. Why the high concentration of cadmium present in the bone tissues? Cadmium accumulates in it for long term of years. The Cd rich bone easily damaged by very weak impact. The normal bone mainly formed by Ca-hydroxyapatite with some connective protein tissues. Cadmium containing one formed by the hydroxyapatite, too. There is no apparent change in the nature and crystalline change.

Introduction

Many reports have been recently published on the concentration of trace elements in human organ tissues (Tipton, et al., 1966 and 1969; Yegyu et al. 1970; Terai et al. 1979; Yukawa and et al. 1980; Nishiyama et al., 1985). There also were many reports on the concentration of trace elements in human bones tissues (Hamilton and et al., 1972; Nishiyama et al., 1985; Fulton et al., 1986). In Japan, high cadmium content in bone tissue is characteristic significance. The Itai-itai disease is caused by accumulation of Cd in the bone tissue and other soft tissues. This sickness fell mainly in old female persons. In this study, we reported the trace elemental contents in the bone of
old person that was determined by neutron activation analysis. High concentration of cadmium was found in the bone. This present paper is to obtain information on the accumulation mechanism of cadmium to the old person's bone. Hydroxyapatite that is one of main constituents in human bone. To make clear the accumulation mechanism of Cd in the old person's bone, hydroxyapatite was synthesized at room temperature.

Experimental

Sample: The bone samples were collected from autopsy at Kanto Rosai Hospital. Table 1 shows age, sex of the patients. The sample was sliced and dried in the desiccator with $P_2O_5$. The dried bone sample about 20-30 mg was cut correctly out and put in polyethylene bag.

<table>
<thead>
<tr>
<th>No.</th>
<th>Age</th>
<th>Sex</th>
<th>No.</th>
<th>Age</th>
<th>Sex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
<td>male</td>
<td>12</td>
<td>48</td>
<td>female</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
<td>female</td>
<td>13</td>
<td>50</td>
<td>male</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>male</td>
<td>14</td>
<td>52</td>
<td>male</td>
</tr>
<tr>
<td>4</td>
<td>33</td>
<td>female</td>
<td>15</td>
<td>54</td>
<td>male</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
<td>male</td>
<td>16</td>
<td>57</td>
<td>male</td>
</tr>
<tr>
<td>6</td>
<td>37</td>
<td>male</td>
<td>17</td>
<td>63</td>
<td>male</td>
</tr>
<tr>
<td>7</td>
<td>42</td>
<td>male</td>
<td>18</td>
<td>64</td>
<td>male</td>
</tr>
<tr>
<td>8</td>
<td>44</td>
<td>male</td>
<td>19</td>
<td>68</td>
<td>male</td>
</tr>
<tr>
<td>9</td>
<td>46</td>
<td>female</td>
<td>20</td>
<td>73</td>
<td>male</td>
</tr>
<tr>
<td>10</td>
<td>47</td>
<td>male</td>
<td>21</td>
<td>76</td>
<td>female</td>
</tr>
<tr>
<td>11</td>
<td>48</td>
<td>male</td>
<td>22</td>
<td>76</td>
<td>female</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23</td>
<td>81</td>
<td>female</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24</td>
<td>81</td>
<td>female</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>87</td>
<td>male</td>
</tr>
</tbody>
</table>

Table 1 Identities of osteoporotic patients(12-25)

Determination: The concentrations of trace elements in the bone samples were determined by neutron activation analysis. Such short lived nuclides as $^{49}$Ca, $^{65}$Cu, $^{28}$Mg, $^{42}$K, $^{38}$Cl and $^{23}$Na were irradiated for 2 min by neutron at neutron flux of $1.5 \times 10^{12}$ n cm$^{-2}$ s$^{-1}$, 3 min cooling and 3 min determination of $\gamma$-ray spectra. Long lived nuclides as $^{115}$Cd, $^{60}$Co, $^{52}$Cr, $^{56}$Fe, $^{75}$Se and $^{65}$Zn were irradiated for 24 hours at neutron flux of $5 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$. After decay of $^{23}$Na $\gamma$-ray spectrum was determined for 5000 s. Phosphorus was determined by ICP-AES.

Synthesize hydroxyapatite: Hydroxyapatite was synthesized by following method. Ammonium basic solution (pH12) of calcium nitrate tetrahydrate added dropwise to ammonium basic solution (pH12) of ammonium phosphate dibasic($\left(\text{NH}_4\right)_2\text{HPO}_4$) taking for 12 hours. After whole solution mixing, the solution was boiled for 3 min and the produced precipitation was separated from the solution by No.4 filter-paper. The precipitation was washed by 250 ml boiled pure water. It was dried in the electric dry-box at 110 C for 24 hours over.
Table 2. The concentration of trace elements in human bone. (μg/g; dry wt.)

<table>
<thead>
<tr>
<th>No.</th>
<th>SX</th>
<th>AG</th>
<th>Ca*</th>
<th>Cd</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe*</th>
<th>Mg*</th>
<th>Mn</th>
<th>K*</th>
<th>P*</th>
<th>Se</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M</td>
<td>21</td>
<td>7.97</td>
<td>22.1</td>
<td>3.26</td>
<td>0.403</td>
<td>12.7</td>
<td>0.369</td>
<td>480</td>
<td>3.47</td>
<td>---</td>
<td>3.78</td>
<td>7.96</td>
<td>372</td>
</tr>
<tr>
<td>2</td>
<td>F</td>
<td>28</td>
<td>110</td>
<td>92.3</td>
<td>21.6</td>
<td>0.258</td>
<td>8.11</td>
<td>2.3</td>
<td>433</td>
<td>14.7</td>
<td>---</td>
<td>43.0</td>
<td>2.97</td>
<td>1440</td>
</tr>
<tr>
<td>3</td>
<td>M</td>
<td>29</td>
<td>125</td>
<td>20.5</td>
<td>12.0</td>
<td>0.213</td>
<td>42.5</td>
<td>1.49</td>
<td>977</td>
<td>11.1</td>
<td>---</td>
<td>56.5</td>
<td>---</td>
<td>826</td>
</tr>
<tr>
<td>4</td>
<td>F</td>
<td>33</td>
<td>16.7</td>
<td>99.3</td>
<td>6.95</td>
<td>0.328</td>
<td>6.97</td>
<td>0.617</td>
<td>64.1</td>
<td>9.85</td>
<td>---</td>
<td>8.60</td>
<td>3.25</td>
<td>641</td>
</tr>
<tr>
<td>5</td>
<td>M</td>
<td>35</td>
<td>69.0</td>
<td>24.0</td>
<td>2.24</td>
<td>0.494</td>
<td>3.37</td>
<td>0.227</td>
<td>171</td>
<td>4.41</td>
<td>---</td>
<td>27.5</td>
<td>13.1</td>
<td>252</td>
</tr>
<tr>
<td>6</td>
<td>M</td>
<td>37</td>
<td>20.8</td>
<td>49.5</td>
<td>58.5</td>
<td>---</td>
<td>5.78</td>
<td>5.12</td>
<td>146</td>
<td>3.41</td>
<td>---</td>
<td>14.1</td>
<td>13.2</td>
<td>588</td>
</tr>
<tr>
<td>7</td>
<td>M</td>
<td>42</td>
<td>13.7</td>
<td>113</td>
<td>14.2</td>
<td>---</td>
<td>14.0</td>
<td>1.82</td>
<td>384</td>
<td>14.4</td>
<td>0.307</td>
<td>35.8</td>
<td>3.70</td>
<td>889</td>
</tr>
<tr>
<td>8</td>
<td>M</td>
<td>44</td>
<td>81.9</td>
<td>6.57</td>
<td>3.96</td>
<td>---</td>
<td>7.28</td>
<td>0.391</td>
<td>386</td>
<td>5.90</td>
<td>0.187</td>
<td>36.3</td>
<td>13.8</td>
<td>293</td>
</tr>
<tr>
<td>9</td>
<td>F</td>
<td>46</td>
<td>42.5</td>
<td>63.2</td>
<td>22.0</td>
<td>0.846</td>
<td>7.70</td>
<td>2.751</td>
<td>196</td>
<td>15.6</td>
<td>0.727</td>
<td>21.5</td>
<td>5.72</td>
<td>2080</td>
</tr>
<tr>
<td>10</td>
<td>M</td>
<td>47</td>
<td>24.1</td>
<td>110</td>
<td>5.08</td>
<td>0.759</td>
<td>8.45</td>
<td>0.629</td>
<td>66.6</td>
<td>6.13</td>
<td>---</td>
<td>11.4</td>
<td>---</td>
<td>505</td>
</tr>
<tr>
<td>11</td>
<td>M</td>
<td>48</td>
<td>203</td>
<td>85.9</td>
<td>10.2</td>
<td>11.5</td>
<td>10.4</td>
<td>0.273</td>
<td>829</td>
<td>3.29</td>
<td>1.75</td>
<td>79.4</td>
<td>68.5</td>
<td>368</td>
</tr>
<tr>
<td>12#</td>
<td>F</td>
<td>48</td>
<td>90.7</td>
<td>314</td>
<td>6.60</td>
<td>0.621</td>
<td>24.8</td>
<td>0.616</td>
<td>396</td>
<td>12.9</td>
<td>---</td>
<td>42.0</td>
<td>0.391</td>
<td>1280</td>
</tr>
<tr>
<td>13#</td>
<td>M</td>
<td>50</td>
<td>72.5</td>
<td>19.3</td>
<td>20.9</td>
<td>9.09</td>
<td>7.44</td>
<td>1.36</td>
<td>391</td>
<td>11.4</td>
<td>2.29</td>
<td>34.0</td>
<td>58.0</td>
<td>317</td>
</tr>
<tr>
<td>14#</td>
<td>M</td>
<td>52</td>
<td>15.5</td>
<td>167</td>
<td>27.7</td>
<td>5.98</td>
<td>44.5</td>
<td>2.32</td>
<td>115</td>
<td>3.37</td>
<td>3.13</td>
<td>10.8</td>
<td>36.0</td>
<td>353</td>
</tr>
<tr>
<td>15#</td>
<td>M</td>
<td>54</td>
<td>12.3</td>
<td>80.7</td>
<td>8.53</td>
<td>4.93</td>
<td>3.53</td>
<td>0.533</td>
<td>102</td>
<td>4.73</td>
<td>0.65</td>
<td>9.13</td>
<td>29.3</td>
<td>417</td>
</tr>
<tr>
<td>16#</td>
<td>M</td>
<td>57</td>
<td>18.0</td>
<td>43.2</td>
<td>9.71</td>
<td>10.9</td>
<td>7.17</td>
<td>0.345</td>
<td>83.6</td>
<td>4.54</td>
<td>1.96</td>
<td>8.60</td>
<td>65.0</td>
<td>243</td>
</tr>
<tr>
<td>17#</td>
<td>M</td>
<td>63</td>
<td>60.0</td>
<td>142</td>
<td>15.8</td>
<td>8.28</td>
<td>13.4</td>
<td>0.957</td>
<td>416</td>
<td>15.2</td>
<td>1.37</td>
<td>27.5</td>
<td>49.6</td>
<td>1820</td>
</tr>
<tr>
<td>18#</td>
<td>M</td>
<td>64</td>
<td>61.7</td>
<td>85.7</td>
<td>14.7</td>
<td>9.44</td>
<td>14.4</td>
<td>0.657</td>
<td>263</td>
<td>5.47</td>
<td>3.23</td>
<td>29.5</td>
<td>85.2</td>
<td>387</td>
</tr>
<tr>
<td>19#</td>
<td>M</td>
<td>68</td>
<td>47.5</td>
<td>43.2</td>
<td>11.5</td>
<td>7.46</td>
<td>14.5</td>
<td>0.626</td>
<td>171</td>
<td>2.63</td>
<td>1.29</td>
<td>18.7</td>
<td>43.6</td>
<td>321</td>
</tr>
<tr>
<td>20#</td>
<td>M</td>
<td>73</td>
<td>74.4</td>
<td>19.0</td>
<td>41.8</td>
<td>12.4</td>
<td>10.1</td>
<td>3.13</td>
<td>580</td>
<td>22.4</td>
<td>3.44</td>
<td>32.1</td>
<td>78.1</td>
<td>465</td>
</tr>
<tr>
<td>21#</td>
<td>F</td>
<td>76</td>
<td>15.2</td>
<td>15.3</td>
<td>6.23</td>
<td>5.83</td>
<td>5.34</td>
<td>0.185</td>
<td>161</td>
<td>3.55</td>
<td>0.681</td>
<td>16.4</td>
<td>34.2</td>
<td>171</td>
</tr>
<tr>
<td>22#</td>
<td>F</td>
<td>76</td>
<td>90.8</td>
<td>515.8</td>
<td>40.6</td>
<td>24.6</td>
<td>14.7</td>
<td>2.78</td>
<td>362</td>
<td>32.3</td>
<td>1.76</td>
<td>44.4</td>
<td>144</td>
<td>2150</td>
</tr>
<tr>
<td>23#</td>
<td>F</td>
<td>81</td>
<td>185</td>
<td>73.8</td>
<td>21.0</td>
<td>16.8</td>
<td>12.8</td>
<td>1.01</td>
<td>790</td>
<td>16.3</td>
<td>3.30</td>
<td>75.5</td>
<td>97.8</td>
<td>755</td>
</tr>
<tr>
<td>24#</td>
<td>M</td>
<td>87</td>
<td>43.0</td>
<td>66.4</td>
<td>9.68</td>
<td>4.89</td>
<td>6.29</td>
<td>0.827</td>
<td>358</td>
<td>23.0</td>
<td>0.058</td>
<td>19.5</td>
<td>31.9</td>
<td>616</td>
</tr>
<tr>
<td>25#</td>
<td>F</td>
<td>81</td>
<td>152</td>
<td>309</td>
<td>5.16</td>
<td>---</td>
<td>11.9</td>
<td>0.517</td>
<td>673</td>
<td>48.4</td>
<td>---</td>
<td>66.7</td>
<td>---</td>
<td>2510</td>
</tr>
</tbody>
</table>

* : mg/g. #: osteoporotic patients.
Results and Discussion

The result of determination of trace elements in the bone was shown in table 2. The most high concentration (515 g/g) of cadmium is found in 76 years old female patient and the most low concentration (6.57 g/g) is found in 44 years old male patient. However this later patient has not the osteoporosis. Mean value of cadmium content is 135±141 g/g for osteoporosis patients. That of younger patients (21-48 years old) shows the value 62.4 ± 37.9 g/g. Both mean values have great standard variation, because the analytical data have large dissolution. The mean value of osteoporotic patients is higher than that of younger patients. There is significant difference between both the mean values. Ratio of Ca$^{10}$ and (PO$_4$)$_6$ that is constituent balance of hydroxyapatite, is calculated from the analytical data of Ca and P. The result is shown in table 3. The ratio of Ca$^{10}$ and (PO$_4$)$_6$ is 1.425 on the ordinary constituents balance of hydroxyapatite. Almost ratio is lower than that of ordinary hydroxyapatite. Mean value of ratio (1.077) of osteoporotic patients is slightly higher than that (1.168) of younger patients.

Table 3  Ratio of Ca$^{10}$ and (PO$_4$)$_6$
calculated from the analytical data.

<table>
<thead>
<tr>
<th>No.</th>
<th>Ca$^{10}$/PO$_4$</th>
<th>No.</th>
<th>Ca$^{10}$/PO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.146</td>
<td>13</td>
<td>1.159</td>
</tr>
<tr>
<td>2</td>
<td>1.202</td>
<td>14</td>
<td>0.780</td>
</tr>
<tr>
<td>3</td>
<td>1.390</td>
<td>15</td>
<td>0.732</td>
</tr>
<tr>
<td>4</td>
<td>1.055</td>
<td>16</td>
<td>1.138</td>
</tr>
<tr>
<td>5</td>
<td>1.364</td>
<td>17</td>
<td>0.988</td>
</tr>
<tr>
<td>6</td>
<td>0.802</td>
<td>18</td>
<td>1.181</td>
</tr>
<tr>
<td>7</td>
<td>1.119</td>
<td>19</td>
<td>1.381</td>
</tr>
<tr>
<td>8</td>
<td>1.226</td>
<td>20</td>
<td>1.260</td>
</tr>
<tr>
<td>9</td>
<td>1.074</td>
<td>21</td>
<td>0.504</td>
</tr>
<tr>
<td>10</td>
<td>1.149</td>
<td>22</td>
<td>1.109</td>
</tr>
<tr>
<td>11</td>
<td>1.424</td>
<td>23</td>
<td>1.332</td>
</tr>
<tr>
<td>12</td>
<td>1.174</td>
<td>24</td>
<td>1.239</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>1.198</td>
</tr>
</tbody>
</table>

The Ca$^{10}$/(PO$_4$)$_6$ value of younger patients is near by the standard value (1.425). This means that the bone of younger patients is more solid than the bone of osteoporotic patients. Another characteristic fact is that the Ca content of the osteoporotic patients is lower than that of younger patients.

Figure 1 shows the cadmium contents against Ca$^{10}$/(PO$_4$)$_6$ values. Points almost centers near the concentration of Cd 100 ppm.

How cadmium enriches in the bone structure? The results of hydroxyapatite synthesis coexist with cadmium shown in table 4. By the results, cadmium easily enters almost quantitatively to the structure of hydroxyapatite. The ionic radius of calcium is 0.99Å and cadmium 0.97Å. Both ionic radii are very similar and
other chemical properties are resemble like atomic valence.

On this study, the enrichment mechanism of cadmium in the osteoporotic bone is explained as follows. Old person takes less daily calcium and absorbs less calcium on small intestine. When human body is deficient in calcium, it demands calcium or similar elements. One of them is cadmium and it relatively exists in many organ tissues. Thus, cadmium enriches in the human bone for very long term or may some decades. As cadmium enriched in the bone can not metabolite with calcium, it does not excrete from body and enriches in the bone.

References

Nishiyama, K. et al.; Grand in Aid for Scientific Research Cooperative Research (A) 5730014.
Yagyu, H., et al.; Tokyo Toritsu Eisei Kenkyusho Kenkyu Nenpo, 22:188
HIGH QUALITY NEUTRON RADIOGRAPHY IMAGING USING COOLED CCD CAMERA – TOMOGRAPHY –

Hisao KOYABASHI

Institute for Atomic Energy, Rikkyo University, 2-5-1 Nagasaka, Yokosuka, Kanagawa, 240-01, Japan.

ABSTRACT

An electronic imaging technique using cooled charge-coupled-device camera (C-CCD) was applied to neutron radiography. The camera was examined for linearity of signal outputs and its dynamic ranges about the number of photons generated in a converter by an incident neutron beam. It is expected that the camera can be applied to high quality NR imaging especially to tomographic imaging for static objects. When the C-CCD camera is applied to get tomogram on the basis of its excellent characteristics, the results will be discussed about the quality of the image through a dynamic range of CT value which is defined in this paper, and a guide of dimensional limitation which can reasonably reconstruct tomograms.

I. INTRODUCTION

Since 1990, a cooled charge-coupled-device camera (C-CCD; Hamamatsu C3140, 510×492×12 bits, −40°C) has been applied to neutron radiography (NR) using Rikkyo Research Reactor (RUR; TRIGA-II) by Kobayashi et al.[1,2] A magnitude of the camera output was directly proportional to number of incident photons on the CCD chip and a wide dynamic range was found. Furthermore, positions of incident photons were accurately recorded without distortion on the CCD chip. The results show that the camera can be applied to a precision dimensional measurement for a static object.

They have also successfully applied the camera to determine effective total macroscopic cross sections (Σ) through measurements of transmittance for several materials with given neutron beam.[2,4] In those studies, it was noted that signals originated by scattered neutrons and gamma-rays give a distortion on the linearity of NR signal intensity as position dependent offset signals. They have shown that the scattered neutron and the gamma-ray noise components can be approximated as signals measured at behind of samples with a neutron opaque material and easily subtracted. The method has been extended to two dimensionally.[5]

It has been also expected that the C-CCD should be applied to neutron tomography[1,2] based on the excellent characteristics which are essentially required to get a high quality tomogram. Recently, these advantages have been utilized to a tomography reconstructed from two dimensional projection images.[6–8] Kobayashi[6] has showed
excellent linearity of the CT value and proved the additive validity of the C-CCD. The range of the linearity should be defined by a dynamic range of the C-CCD output. A statistical character of the camera output signal should related to the quality of NR images especially to tomograms. McFarland et al.\cite{7,8} have analyzed a statistical character of the C-CCD output.

In this study, analyses of the C3140 C-CCD camera are further examined on a basis of experimental data. The results is extended to define qualities of tomograms. An idea of effective product is proposed to characterize of a tomographic system being related to quantities of CT values and maximum sample thickness which is able to properly reconstruct.

II. EXPERIMENTAL

2.1 NR FACILITIES

Two neutron beams with different intensities are formed by a multipurpose collimator assembly which is installed in the tangential beam port in the RUR (TRIGA-II, 100kW).\cite{2} Diaphragms were selected to be 29 mmφ and 86.3 mmφ in this study and corresponding L/D value were 100 and 35.2, respectively, at the imaging position. In the arrangement, neutron fluxes were measured using gold foil method and found to be \(1.5 \times 10^6\) n/cm\(^2\)-s and \(1.24 \times 10^7\) n/cm\(^2\)-s, respectively.

The reduction of gamma-ray background irradiated into the CCD chip is imperative to lower irregular noise and strong white spot noises. A double-mirror optics was used between the converter screen and the lens. Furthermore, the C-CCD was surrounded completely with lead blocks of more than 10 cm in thickness. Thus, the quality of the C-CCD image and the dynamic range of NR signals were much improved to an acceptable level.

2.2 CAMERA AND ELECTRONICS

The CCD chip installed in the C3140 cameras can be cooled down to \(-40^\circ\)C by a three stage Peltier element. The chip is an interline type (SONY; IVX018-L) and has effective area of 8.8mm\(^2\)×6.6mm\(^2\). Number of pixels are \(510^2\)×492\(^2\) having a pitch of 17\(\mu\)m\(^2\)×13\(\mu\)m\(^2\). A signal output of each pixel is converted to a 12 bit data by an analog-to-digital converter. The camera is connected with an image processor (Hamamatsu C3366). The C3366 is interfaced with RS422 to a host computer (NEC: PC9801 personal processor) which is connected by a 320 MB hard disk with a 640 MB magneto-optical disk memory (Mitsui HD/MO Twin System, HM5050). NR images were stored as the data size of 512×512×16bit(−0.5MB) on the hard disk.

A high speed workstation (SUN SPARC station-2 with 28.5 MIPS) was used for further image processing of reconstruction of tomograms. The workstation consists a 64 MB main memory and a 2 GB hard disk memory. All imaged data with the 12 bit length were treated as a 15 bit data length on 512×512 memory planes by the workstation. Results were displayed as 24 bit RGB data on a 19 inch full color monitor.

2.3 IMAGING SYSTEM AND OPTICS

A fluorescent converter using ZnS(Ag) with \(^6\)LiF (Kasei Optronics NRC; emission
peak at 450 nm) was placed on the imaging position of the double mirror optical box. The converter is applicable to the C-CCD, since the sensitivity covers a wavelength range from 400 nm to 1100 nm with a maximum at 530 nm.

A micro-focus lens (f=55 mm F=2.8 Micro-Nikkor) was mounted on the C-CCD camera head. The camera head were set inside of the gamma shield at a working distance of 91 cm. The magnification factor was 12.7 as a ratio of the image size at the chip surface to the real size on the converter.

2.4 SIGNAL INTENSITY AND STATISTICAL CHARACTER

In our experimental arrangement, single gray scale output corresponds to 185 neutrons incident into an area of the converter 216×165 μm² which is equivalent to the pixel area. And then, number of photons generated in the converter was estimated to be 0.7×10⁵ photons per neutron which is less than a factor two with the estimation of McFarland et al. Where quantum efficiency of CCD, transmission of lens, and reflectance of a mirror were assumed to be 0.35, 0.85, and 0.9, respectively.

The maximum signal as a gray scale level of 4096 was found for the C3140 with a low amplification gain mode (25 electrons/pixel) at 150 sec on-chip integration time at 1.2×10⁷n/cm²-s. Excellent linearity was found between the NR signal after subtraction of back ground signals. When the integration time was selected to be 140 sec, total counts of 3897 in gray scale was obtained as an average value. In this case, back ground signals consisted of a back scattering component (566 counts), gamma-ray induced dark current component (52 counts), dark current (22 counts) at -40°C, and an offset

---

Fig.1 A sectional diagram of the object designed to test linearity of the CT value.
signal (55 counts). The observed signals were averaged over 10×10 pixels. Standard deviation was found to be ±0.42% (14 gray scale) at net signal (3209 counts) and dynamic range was estimated to be 230:1 in this case.

2.5 DESCRIPTION OF SAMPLE FOR TOMOGRAPH

An object was designed to test the linearity of CT-value and fabricated using materials with different Σ from 0.1cm⁻¹ to 2.5cm⁻¹ (fig.1). The rotation axis of the object was adjusted and fixed vertically to the floor and perpendicularly to the beam axis. The object was rotated from 0 to 360 degrees with every step of 2 degrees during experiments. Thus, two dimensional 180 projection images were obtained.

To estimate scattered neutron components, a grid with three cadmium strips (5mm×0.5mm-t) were placed in front of the object and on a plane perpendicular to the beam axis. And, the plane was set at 7 cm in front of and parallel to the imaging plate. Signal intensities in the shadow regions of the strips were approximated to scattered neutron component including gamma-ray background and dark current. Two dimensional scattered neutron components were estimated for shading and individual object images by interpolation under assumption of a parabolic function.

The 180 projection images, two shading images and six background images were transferred to the workstation for further image processing of reconstruction.

III. RESULTS AND DISCUSSIONS

3.1 TOMOGRAPHY

In addition to regular preliminary process, additive treatments of projection data were required before start the reconstruction processing.

(1) White spots generated mainly by gamma-rays were extinguished for all NR images using a 3×3 matrix intelligent filter without any data deteriorations except for the spot.

(2) Two dimensional scattered neutron components were estimated for every projection and shading images, and subtracted.

(3) All 180 (360°) projection images were folded at the angle 180° and averaged for complementary pair (θ and 2π-θ) of images. So, geometrical unsharpness were averaged.

(4) In a reconstructed tomographic image, several techniques have been proposed to improve image quality. A simple one is based on an interpolation of projection data. Two adjoined projection images were averaged and assumed to be images at middle angles of those two projection images. The original 90 projection and the additive 90 pseudo-projection images were used as a set of 180° rotation data with one degree step to following reconstruction process.

After finished the pre-processings, a convolution algorithm was applied with Shepp and Logan filter⁹¹ to the sinograms. A stack of tomograms was obtained, and were stored on the hard disk memory as a set of sliced data except for shadow regions of Cd strips. At present stage, a reconstructed image can be displayed as a 15 bit gray scale only for a selected horizontally sliced plane on the full color monitor. One of tomogram is shown at a slice number 250 in fig.2. Sizes and shapes for all materials are reconstructed with a high quality image. It is noted that the figure shows not only the complicated shape of the dry wood but also the growth ring pattern.
Fig. 2 Tomogram of the CT test sample reconstructed from the 180 pseudo-one-degree-step projection images at the slice number 250.

3.2 LINEARITY AND RESOLUTION OF CT VALUE

Important measure of characteristics in tomographic image are a linearity of the CT value defined by a relation $\langle \Sigma \rangle = \langle d\ln(l)/dr \rangle$,[4] a resolution of CT value and a spatial resolution of the tomographic image.

The CT value has been defined by our previous paper[6] as the experimentally determined $\langle \Sigma \rangle$ magnified by a factor 1000, and then,

$$CT = 935 \times \frac{| \text{measured } \langle \Sigma \rangle \text{ of object} - \text{measured } \langle \Sigma \rangle \text{ of Al} |}{| \text{measured } \langle \Sigma \rangle \text{ of Fe} - \text{measured } \langle \Sigma \rangle \text{ of Al} |} + 93.$$  

(1)

Where constants are derived from two $\langle \Sigma \rangle$ of Fe and Al. The normalized CT values for Fe and Al magnifies $\langle \Sigma \rangle$ by a factor 1000 are assumed to be 1028±83 and 93±17, respectively, whose values have been obtained by averaging over the values measured at three different thermal neutron beams (Rikkyo:TRIGA/N2, Kyoto:KUR/E2, and JAERI:JRR-3M/TNRF2).[4]
Fig. 3 Reconstructed CT vs. total macroscopic cross sections for various materials.

Results are plotted in Fig. 3 for the slice number 120 (solid circles) and 230 (open circles). Excellent linearity are shown between $\langle \Sigma \rangle$ and CT within statistical uncertainty. The linearity supported the justification of the data process for the all reconstruction steps. In Fig. 2, a part of growth rings in the dry wood stick are clearly shown. For the dry wood, two different $\langle \Sigma \rangle$ values are given by averaged CT of high and low density areas along the growth ring pattern and shown as dotted circles in this figure.

Resolution of CT values were estimated from Fig. 2 as standard deviations and shown in Fig. 3. Typical resolution of CT value was found to be $\pm 5\%$. If the reconstructed image is smoothed, the statistical uncertainty should be much lowered. However, no systematic analysis has been made for an effect of averaging by the 180° folding of projection images (pre-processing step-(3)), and of generation of pseudo-projection images at present stage (pre-processing step-(4)).

3.3 DEFINITION OF DYNAMIC RANGE FOR THE CT VALUE

In addition to the linearity and resolution of CT, a dynamic range of CT is another important parameter to define the quality and the limitation of tomographic imaging. Because the dynamic range can be expressed as functions of $\langle \Sigma \rangle$ and
thickness \( t \) of transmitting sample.

A line integration of CT value along a neutron trajectory is equivalent to an integrated value of a product \( T \) of \( \langle \Sigma(t) \rangle \) and differential thickness \( dt \) of a transmitting material. The product \( T \) is given as a non dimensional quantity and written by,

\[
T = \int \langle \Sigma(t) \rangle dt = 10^{-3} \int C T(t) dt.
\]  

(2)

The product \( T \) is also equivalent to the logarithm of transmittance at the trajectory. Then, an ideal upper limit, **maximum product** \( T_{\text{max}} \) can be described as the case of no transmitting object using an incident neutron intensity \( I_0 \) as,

\[
T_{\text{max}} = \ln(I_0).
\]

(3)

On the other limit of \( T_{\text{max}} \), a **minimum detectable product** \( T_{\text{min}} \) can be defined using a statistical uncertainty \( \delta I_0 \) for \( I_0 \) as,

\[
T_{\text{min}} = \ln(\delta I_0).
\]

(4)

Where white spots were assumed to be completely eliminated by the preprocessing step. The value \( T_{\text{min}} \) depends on the statistical character of NR image which is resulted from statistics of neutron quanta, non-white spot type gamma-ray induced noise, and electronic noises. The value also depends on data processing steps such as smoothing, averaging, frame transforms, domain transforms, and so on. As a result, an **effective product** \( T_{\text{eff}} \) is derived as,

\[
T_{\text{eff}} = T_{\text{max}} - T_{\text{min}} = \ln(I_0/\delta I_0).
\]

(5)

The **effective product** is equivalent to the dynamic range of the system, and define the dynamic range of CT value.

For example, the dynamic range of the system is estimated to be 230 as shown in the section 2.4. Then, the quantity can be converted to be 5.4 of \( T_{\text{eff}} \) by (5). On the other hand, a maximum integrated CT value \( \Sigma(C T, \chi_d) \) is given by a trajectory shown in fig.1 and found to be 4.4 which is satisfy the undeformed condition less than \( T_{\text{eff}} \) for the tomography. In fact, only slight artifact is observed in fig.2 along the same trajectory as shown in fig.1, and reasonable CT values were found for those samples (acrylic resin, copper, aluminum, and iron) along the trajectory as shown in fig.3.

The idea of the effective product is quite useful parameter which gives a guide to the effectiveness and limitation of tomograph. For instance, if \( T_{\text{eff}} \) and \( \langle \Sigma \rangle \) are known for a homogeneous material in advance of experiments. The maximum sample thickness which can reconstructed properly is given by

\[
t_{\text{max}} = T_{\text{eff}}/\langle \Sigma \rangle.
\]

(6)

For inhomogeneous materials, the relation is easily transformed. Therefore, we can expected to a dimensional limit of reconstruction of tomograph by \( t_{\text{max}} \). For example, \( t_{\text{max}} \) of Al, Fe, and Cd is estimated to be 58 cm, 5.4 cm, and 0.045 cm. Therefore, 1 mm Cd thicker than \( t_{\text{max}} \) and the material should arise abnormally strong artifact.
IV. CONCLUSION

The C-CCD camera was successfully extended to apply the high quality tomographic imagerings attainable with their wide dynamic range and with the distortion free imaging for spatial position. The range keeping linearity between effective total macroscopic cross section and CT value should one of fundamental measure of the system validity. The linear relation is found at least in the range from 0.1 cm\(^{-1}\) to 2.5 cm\(^{-1}\). The effective product \(T_{\text{eff}}\) and maximum allowable sample thickness \(t_{\text{max}}\) are defined in this paper, and both values are useful to define dynamic range of CT value and to estimate a limitation of samples for reconstruction.

In JAERI, high quality C-CCD camera C4880 will be introduced near future. The CCD chip of the C4880 is a frame transfer type (Texas; TC-215) and has effective area of 12mm\(^{\text{H}}\times12\text{mm}^{\text{V}}\). Number of pixels are 1000\(^{\text{H}}\times1018\text{V}^{\text{V}}\) having a pitch of 12\(\mu\text{m}^{\text{H}}\times12\text{m}^{\text{V}}\). The signal output of each pixel is converted to a 14 bit gray scale data by an analog-to-digital converter. Therefore, more extensive high quality NR study will be expected by the system in near future.

It is noticed that more extended analyses are required for the effect to statistical character on CT resulted from gamma radiation induced noise, from un-uniform response between pixels, and generated from various steps in the data processing. Our efforts will continue in these field especially to realize more wider dynamic range of CT value and to get artifacts free high quality image using the high performance CCD camera.

This work was partly supported by The Science Research Promotion Fund from Japan Private School Promotion Foundation.

PROMPT GAMMA-RAY ANALYSIS USING JRR-3M COLD AND THERMAL NEUTRON GUIDE BEAMS


Department of Chemistry, Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

*Research Center for Nuclear Science and Technology, The University of Tokyo
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

A permanent and stand-alone neutron-induced prompt gamma-ray analysis (PGA) system, usable at both cold and thermal neutron beam guides of JRR-3M has been constructed. Neutron flux at the sample positions were $1.4 \times 10^8$ and $2.4 \times 10^7$ n cm$^{-2}$ s$^{-1}$ for the cold and thermal neutrons, respectively. The $\gamma$-ray spectrometer is equipped to acquire three modes of spectra simultaneously: single mode, Compton suppression mode and pair mode, in an energy range up to 12 MeV. Owing to the cold neutron guide beam and the low $\gamma$-ray background system, analytical sensitivities and detection limits better than those in other PGA systems have been achieved. Analytical sensitivity and detection limit for 73 elements were measured. Boron, Gd, Sm and Cd are the most sensitive elements with detection limits down to 1 to 10 ng. For some elements such as F, Al, V, Eu and Hf, decay $\gamma$-rays are more sensitive compared to their respective prompt $\gamma$-ray. Analytical sensitivity of several heavy elements through detection of characteristic X-rays was higher than that through the prompt $\gamma$-ray detection. Analytical applicability of some sensitive elements such as B, H, Gd and Sm were examined. Isotopic analysis of Ni and Si were also examined.

INTRODUCTION

A neutron-induced prompt $\gamma$-ray analysis (PGA)$^{1,2}$ is an elemental and isotopic analytical technique in which prompt $\gamma$-rays emitted within $10^{-14}$ s after neutron capture reactions are measured. The PGA is characterized by its capability for nondestructive multi-elemental analysis and by its ability for analyzing H, B, N, S, P, Si and Cd which are difficult to be analyzed by instrumental neutron activation analysis (INAA). Owing to poor beam quality previous PGA$^{3-5}$ had disadvantages of low analytical sensitivity and high detection limit. The PGA has thus been regarded only as complementary to INAA. Earlier studies$^{6-8}$ indicated that PGA using a neutron guide beam has improved analytical sensitivity and detection limit. A permanent and stand-alone PGA system, usable at both cold and thermal neutron beam guides of JRR-3M has been constructed$^{9-11}$, similar to the National Institute of Standards and Technology (NIST)$^{12}$ and Research Center (KFA) Jülich$^{13}$. The design concept is to achieve the lowest $\gamma$-ray background. To achieve this, 1) neutron shielding materials, lithium fluoride (LiF) tiles and fluorocarbon resin, are used as construction materials at positions near the sample, 2) the sample box is filled with He gas, and 3) Ge-BGO detectors are used to lower the
Compton background. In this paper, characteristics of the system and application of PGA for elemental and isotopic analysis are described.

**EXPERIMENTAL**

**Apparatus**

The PGA system can be set either at the cold (C2-3-2) or thermal (T1-4-1) neutron beam guide of JRR-3M (20 MW). The specification of the system is shown in Table 1. The cold neutrons are guided from a liquid hydrogen cold neutron source to the PGA system through a 51 m Ni coated glass mirror tube. The thermal neutrons are guided from the heavy water region through a 60 m Ni coated glass mirror tube and a 3.17 m evacuated guide tube. Initially, the present system was set behind a 4 m extended guided tube at the cold neutron beam port (C2-3-2)\(^{10,11}\). For improving neutron flux and homogeneity, the system has been modified and set directly to the cold neutron guide without the extended guided tube.

**Table 1 Specifications of the prompt \( \gamma \)-ray analyzing system of JRR-3M**

<table>
<thead>
<tr>
<th>Neutron beam</th>
<th>Cold neutron</th>
<th>Thermal neutron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux, ( \text{n cm}^{-2} \text{s}^{-1} )</td>
<td>1.4 \times 10^8</td>
<td>2.4 \times 10^7</td>
</tr>
<tr>
<td>Energy, meV (Å)</td>
<td>3.0 meV (5.2 Å)</td>
<td>15 meV (2.3 Å)</td>
</tr>
<tr>
<td>Beam size, mm(^2)</td>
<td>20 \times 20</td>
<td>20 \times 20</td>
</tr>
<tr>
<td>Sample to Ge detector</td>
<td>29.5</td>
<td>24.5</td>
</tr>
<tr>
<td>distance, cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \gamma )-ray spectrometer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge detector</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BGO detector (Crystal size)</td>
<td>n-Type HpGe, FWHM: 1.75 keV (at 1332 keV), Relative efficiency: 23.8 % (at 1332 keV). Main: 171 mm( \phi ) x 206 mm long, 20–39 mm thick Catcher: 60.3 mm( \phi ) x 60 mm long</td>
<td>MCA: SEIKO EG &amp;G model 7800, 4 8 k ADCs</td>
</tr>
<tr>
<td>Pulse height analyzer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurement mode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atmosphere in the sample box</td>
<td>Single, Compton suppression, Pair</td>
<td>He</td>
</tr>
</tbody>
</table>

The system consists of a neutron beam shutter, a neutron beam collimator, a sample box, a neutron beam stopper, shielding for neutrons and \( \gamma \)-rays, and a multi-mode \( \gamma \)-ray spectrometer. The neutron beam collimator is made of lithium fluoride (LiF) tiles and its hole size is 20 \( \times \) 20 mm\(^2\). The neutron beam can be stopped by the beam shutter and beam stopper made of 10 mm thickness of sintered boron carbide (B\(_4\)C). The 478 keV prompt \( \gamma \)-rays from B are absorbed by Pb in the shutter and stopper. An air-tight sample box made of polytetrafluoroethylene (PTFE, Teflon) is placed behind the collimator. The emitted prompt \( \gamma \)-rays are detected through a 5 mm thick \( \text{PF}_2\) (95.4 % enrichment) tile. In order to reduce the \( \gamma \)-ray background, which is formed by neutrons scattered at the sample and absorbed by the construction materials, shielding was provided using 2 and 3 cm thick LiF tiles of natural isotopic composition and 5 and 10 cm thick Pb. Neutron and \( \gamma \)-ray shielding around the beam stopper and beam collimator is provided with 1 cm thick rubber containing 20 % B\(_4\)C, 5 or 8 cm thick Fe, and 3 or 5 cm thick Pb. The detector system is surrounded by 10 cm thick Pb shielding. The prompt \( \gamma \)-rays from the sample pass through a 2.0 cm diameter Pb collimator of 10 cm thick and enter the detector.

The multi-mode \( \gamma \)-ray spectrometer consists of a closed end coaxial type high purity Ge detector, BGO (bismuth germanate, Bi\(_4\)Ge\(_3\)O\(_{12}\)) shielding detectors, and a pulse height analyzer (PHA) system controlled by a personal computer. The BGO shielding detectors are
composed of a main shield, which surrounds the detector axially, and a back-shield (catcher). Three modes of prompt γ-ray measurements: a single mode, a Compton suppression mode, and a pair mode, in the energy range of 0 to 12 MeV, can be performed simultaneously. The Ge detector is set with its axis perpendicular to the neutron beam at a distance 29.5 cm (for the cold neutron beam) and 24.5 cm (for the thermal neutron beam). The Ge detector is surrounded by BGO main and catcher detectors which are used as guard detectors for Compton suppression and pair mode spectra. Signals of the three modes are fed into a 8192-channel analog to digital converter (ADC, SEIKO EG&G 1850). All the signals from the ADCs are sorted by a multi-channel analyzer (MCA, SEIKO EG&G model 7800). A more complete description of the PGA system can be found elsewhere. Energy calibration of the γ-ray spectrometer was carried out using decay γ-rays of 56Co and prompt γ-rays of Fe.

Neutron beams were monitored continuously by measuring scattered neutrons with a 3He counter set beside the sample box and also by measuring prompt γ-rays with 0.05 and 0.5 mm thick of Ti plates for the cold and thermal neutrons, respectively. Prompt γ-ray energies and intensities of elements were taken from data compiled by Lone et al.

Analytical procedure

A known amount of sample is wrapped in 25 μm thick fluorinated ethylene propylene resin (FEP) film of an area smaller than 15 × 15 mm² and heat sealed. The wrapped sample is set on a PTFE sample holder by using PTFE string of 0.3 mm (diameter) and is then placed in an air-tight PTFE sample box. The air in the box was purged using He gas flow. The three modes of γ-ray spectra in the energy range of 0 to 12 MeV are acquired for 500 to 50000 s while passing He into the box at a flow rate of about 1000 ml/min.

RESULTS AND DISCUSSIONS

Neutron beam

The beam position and the beam shape were determined by a neutron radiographic method using Gd converter and X-ray film. The neutron flux at the sample position was measured by setting a 0.0254 mm thick Au foil at 45 degrees to the beam and irradiating for 30 min (cold neutron) or 3 to 15 hr (thermal neutron). The values of activation cross sections of 329 and 163 barns were used for the cold and the thermal neutrons, respectively, determined from neutron energy spectra measured by the time of flight method. The average neutron flux of the cold and thermal neutron beams in the 20 × 20 mm² area were 1.4 × 10⁸ and 2.4 × 10⁷ n cm⁻² s⁻¹ with a coefficient of variation of 18 and 5 % for the cold and thermal neutrons, respectively. Formerly when an extended guide tube was used the neutron flux was 1.1 × 10⁸ n cm⁻² s⁻¹ with a coefficient of variation of 34 % for cold neutron beam. The neutron flux and homogeneity of the neutron beam were improved by positioning the system to the beam port of the cold neutron directly. The flux fluctuation at the sample position of the neutron beam during one reactor operation cycle (26 days) was 1.6 and 1.0 % for the cold and thermal neutrons, respectively.

The gamma-ray spectrometer

The time distribution of Fe prompt γ-rays was measured by a time-to-amplitude converter (TAC, ORTEC 567). The start and stop signals were provided by Ge and BGO, respectively. FWHM and FWTM of the distribution curve were 83.0 and 210 ns, respectively.

In the single mode spectrum full energy peaks, together with the single and double escape peaks, are observed. In the Compton suppression mode the Compton continuum is effectively suppressed to about 13 %. The single and double escape peaks are also decreased to about 10 and 17 %, respectively. Small peaks which are not distinct in the single mode spectrum can clearly be seen in the Compton suppression mode. In the pair mode spectrum only the double and single escape peaks were detected. Ideally, the pair mode is set for the detection of double escape peaks only, however, due to incomplete optical isolation of the nose portion of the main
BGO, single escape peaks can still be detected. Peak assignment of complex prompt $\gamma$-ray spectrum can be resolved by comparing the three modes of spectra.

The absolute efficiency was determined using standard sources of $^{56}$Co, $^{57}$Co, $^{60}$Co, $^{133}$Ba, $^{137}$Cs, $^{152}$Eu, and $^{241}$Am. At high energies, prompt $\gamma$-rays of Fe were used. The high energy efficiency values were normalized to create a continuous absolute efficiency curve. The efficiency of full energy peaks and double and single escape peaks of single mode spectrum is higher by a factor of 2 to 3 than that of other PGA systems. However, at energies below 100 keV no published data is available to compare with ours because other PGA systems cannot detect such low energy $\gamma$-rays. The detection efficiency of double escape peak of the pair mode is also higher by a factor of two than reported by other.

Gamma-ray background

The present system was designed to achieve the lowest possible $\gamma$-ray background by placing the sample in a He atmosphere because the scattering and absorption cross section of He is small. The flux measurements carried out with and without air (in He gas atmosphere) indicated that scattering by air can be as much as 8.5%. The $\gamma$-ray background was reduced drastically as a result of the purging for air.

Table 2 Comparison of $\gamma$-ray background counts of the present system with others

<table>
<thead>
<tr>
<th>Element or nuclide</th>
<th>$E_\gamma$ keV</th>
<th>Background count rate, cps</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Univ. Md-NIST$^a$</td>
</tr>
<tr>
<td>H</td>
<td>2223</td>
<td>0.56</td>
</tr>
<tr>
<td>B</td>
<td>478</td>
<td>0.1</td>
</tr>
<tr>
<td>C</td>
<td>1262</td>
<td>0.0014</td>
</tr>
<tr>
<td>N</td>
<td>1885</td>
<td>0.072</td>
</tr>
<tr>
<td>Na</td>
<td>472</td>
<td>0.057</td>
</tr>
<tr>
<td>Al</td>
<td>1779</td>
<td>0.027</td>
</tr>
<tr>
<td>Cl</td>
<td>517</td>
<td>0.007</td>
</tr>
<tr>
<td>Ti</td>
<td>342</td>
<td>0.063</td>
</tr>
<tr>
<td>Fe</td>
<td>352</td>
<td>0.007</td>
</tr>
<tr>
<td>$^{207}$Bi</td>
<td>569</td>
<td></td>
</tr>
<tr>
<td>$^{207}$Bi</td>
<td>1063</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: University of Maryland-NIST (Ref.15), $^b$: University of Missouri (Ref.15),

The $\gamma$-ray background count rate of the system under cold and thermal neutron beams in a He gas atmosphere is tabulated in Table 2 together with the values of other systems. The background count rates are attributed to prompt and decay $\gamma$-rays of elements in a construction material and in air. Even though these $\gamma$-ray lines appear in the Compton suppression spectrum that was acquired for 50000 s in a He atmosphere, these data are the lowest compared to earlier data. The full background count rate of the cold neutron beam is lower by factors of 166 and 55 compared to the data of the University of Maryland-NIST and University of Missouri, respectively. Furthermore, for N, the present data is lower by a factor of 29 compared to the University Maryland-NIST data. The data of the University of Missouri quoted a detection limit of less than 0.008 cps, which is still higher than that of the present system. The $^{207}$Bi background peak in the present system comes from BGO. In other PGA systems background prompt $\gamma$-rays of H and other elements of the construction materials higher than the present data are reported. This is mainly due to the presence of $\gamma$-rays, fast and epithermal neutrons in the beams of the other systems. In those systems, a large amount of moderating and shielding materials would be required to eliminate undesired neutrons. In the present system, however, such large shielding is not necessary.
For wrapping the sample, materials that produce the lowest possible prompt γ-ray backgrounds have to be used. Fluorocarbon resin is the most suitable for this purpose because the constituent elements C and F will emit prompt γ-ray at low count rates. FEP film was chosen from this viewpoint. Another advantage of using FEP film lies in the ease of sealing by heating.

Analytical sensitivity and detection limit of elements

Standard samples heat-sealed in FEP film were irradiated and the prompt γ-rays were measured for a period of time to produce a statistically sufficient count. Interference-free full energy peaks of high intensity were used for the calculation of sensitivity (cps/mg). From the Compton suppression spectrum of a known amount of FEP film, the 3σ background count in the region corresponding to the prompt γ-ray line of a specified element was estimated to calculate the detection limit. The analytical sensitivities and detection limits of 73 elements were measured. The analytical sensitivities of selected elements are shown in Table 3 and compared with those of other systems (Ref. 4, 8). The detection limits of the selected elements are also shown in Table 4 and indicates a very great improvement compared to other systems by reducing γ-ray background at the detector.

Table 3 Comparison of analytical sensitivity of the present system with others

<table>
<thead>
<tr>
<th>Element</th>
<th>Eγ keV</th>
<th>Univ. Md-NIST a</th>
<th>Univ. Mo b</th>
<th>ILL c</th>
<th>JRR-3M Cold</th>
<th>JRR-3M Thermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>2223</td>
<td>0.86</td>
<td>1.23</td>
<td></td>
<td>3.74</td>
<td>0.417</td>
</tr>
<tr>
<td>B</td>
<td>478</td>
<td>530</td>
<td>759</td>
<td>2700</td>
<td>2620</td>
<td>212</td>
</tr>
<tr>
<td>Cd</td>
<td>558</td>
<td>170</td>
<td>247</td>
<td></td>
<td>405</td>
<td>47.5</td>
</tr>
<tr>
<td>Sm</td>
<td>334</td>
<td>640</td>
<td>740</td>
<td>3700</td>
<td>749</td>
<td>142</td>
</tr>
<tr>
<td>Gd</td>
<td>182</td>
<td>680</td>
<td>956</td>
<td>6900</td>
<td>1560</td>
<td>224</td>
</tr>
</tbody>
</table>

Flux, n cm⁻² s⁻¹
Sample to detector distance, cm

2x10⁸ 5x10⁸ 1.3x10⁸ 1.4x10⁸ 2.4x10⁷
50 75 18 29.5 24.5

a: University of Maryland-NIST (Ref.4), b: University of Missouri (Ref.3),
c: ILL (Ref. 8).

The analytical sensitivities of these elements using cold neutron irradiation are 5.3 to 12 times higher than those using thermal neutron irradiation. The analytical sensitivities of these elements at the cold neutron beam are 1.4 to 2 times higher than those obtained using the extended guided tube (Ref. 10, 11). The sensitivity of the present system at the cold neutron beam is generally higher, up to about 5 times that reported values of the University of Maryland-NIST (Ref. 4) and the University of Missouri (Ref. 3) systems, except for Sm. Since the neutron capture resonance cross section of Sm is large at the epithermal region, the Sm sensitivity of the beam type systems is higher than the present cold neutron beam system. Kerr et al. (Ref. 8) reported higher sensitivity values than the present system for B, Sm, and Gd. The main reason for this is that a Ge detector was used without a Compton suppression detector, and thus it could be positioned nearer to the sample. In the present system we can also remove the Compton suppression detectors and put the Ge detector nearer to the sample, but the prompt γ-ray background count will rise drastically resulting in a poorer detection limit.

Boron, Sm, Gd, and Cd are the elements having the highest analytical sensitivity with detection limits down to 1–10 ng and 10–100 ng, at the cold and thermal neutron beams,
respectively. Mercury, Dy, Eu, Er, Nd, In, Hf, Cl, Sc, Ti, Co, and H can be detected to 0.05~1 μg and 0.3~4 μg at the cold and thermal neutron beams, respectively. Lead, F, C, and Bi have the lowest sensitivity with detection limits in the range of 0.2~2 mg and 1~10 mg, at the cold and thermal neutron beam, respectively. Other elements are considered to have a medium sensitivity, such as V, Yb (and most of the other lanthanoids), Mn, Ag, Ni, Na, K, S, Fe, Si, P, Sn, and N and so on with detection limits ranging from 1~100 μg and 5~600 μg at the cold and thermal neutrons, respectively.

The decay γ-rays at 1634 keV from 20F (T1/2:11.03 s), 1779 keV from 28Al (T1/2:2.2406 min), 1434 keV from 52V (T1/2:3.75 min), 90 keV from 152m2Eu (T1/2:1.600 h), and 21.4 keV from 179m1Hf (T1/2:18.68 s) have much higher sensitivities than the corresponding prompt γ-rays. Characteristic X-rays were detected for heavy elements. The emission of the X-rays is possibly due to internal conversion following the emission of prompt γ-rays. The analytical sensitivity of the X-rays for the elements with atomic weights larger than Ta is higher than that of the prompt γ-rays except for Pt, Hg, Pb, and Bi. Measurement of the characteristic X-rays is therefore useful for the analysis of these heavy elements.

<table>
<thead>
<tr>
<th>Table 4 Detection limits of selected elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>P</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Mn</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Cd</td>
</tr>
<tr>
<td>Sm</td>
</tr>
<tr>
<td>Gd</td>
</tr>
<tr>
<td>Hg</td>
</tr>
</tbody>
</table>

Applications of elemental analysis

The gamma-ray spectra of standard reference material Coal Fly Ash (NIST 1633a) was measured as a means to assess the ability of the present system. Prompt γ-ray peaks of Gd, Sm, Fe, and B are found in the spectrum. The S/N ratio of the present data as compared to that from the University of Maryland-NIST16 system for the same sample was found to be higher by a factor of 4 to 8 for Gd, Fe and B, but for Sm it was only 1.3. A beam type PGA system like that of the University of Maryland-NIST contains γ-rays, fast and epithermal neutrons in the beam, thus the γ-ray background is high, especially in the low energy region. However, the guide beam type system is free of γ-rays, fast and epithermal neutrons, so that S/N ratios for Gd, Fe, and B are much higher. As described by Mackey et al.17 for the case of Sm, its higher resonance capture cross section for epithermal neutrons results in a S/N ratio no better than the data of the University of Maryland-NIST system.

Due to its large neutron capture cross section, the B content in reactor materials must be as low as possible. As mentioned already, the present system was found to have the highest sensitivity for B, thus the analysis of B in reactor grade graphite and Be has been performed. The Doppler-broadened 478 keV prompt γ-ray of B which is emitted as a result of 10B(n, α) 7Li → 7Li (σ = 8387 barn) was observed with a good S/N ratio. The determination of B was done by measuring the counts under the 478 keV photo peak. The 2.0 ppm of B thus determined is in good agreement with the certified value (2 ppm) of the material. The detection limit of B was estimated to be 40 ppb. Further improvement of the detection limit down to 4 ppb is achievable if 1 g of sample is used instead of 0.1 g because the spectrum is almost similar to the FEP background spectrum. The B content in Be which is used as the reflector frame of the Japan Material Testing Reactor (JMATR) has also been measured. The B content was determined by measuring 1.0 g Be for 50000 s in the thermal neutron beam. The result of the
analysis, 3.2 ppm, is in good agreement with the value (2.7 to 3 ppm) determined by emission spectrometric method. The detection limit of B in the sample was 24 ppb.

The analytical sensitivity of rare earth elements such as Gd, Sm, Eu, and Dy is higher than other rare earth elements such as Ce, Y, La, Pr, and Tb by 4 orders of magnitude. Therefore, the present system is useful for the determination of these rare earth elements with high sensitivity which are present in the rare earth elements that have lower sensitivity. High purity cerium(IV) oxide (CeO2 99.99 %, 0.18 g) was analyzed at the cold neutron beam for the purpose. The prompt γ-rays at 182 and 199 keV from Gd, 334 and 439 keV from Sm, 186 keV from Dy and Er, and the decay γ-ray at 90 keV from 152m2Eu were detected in the spectrum. The content of Gd and Sm was determined to be 0.41 and 0.62 ppm, respectively, using the interference free prompt γ-ray peaks at 182 and 334 keV for Gd and Sm, respectively. The detection limits of Gd and Sm in the sample were calculated to be 0.11 and 0.14 ppm, respectively.

As was mentioned by Lindstrom et al.12), neutron guide beam PGA has a potential usefulness for trace determination of H in various types of materials. Our system has detection limits for H of 1.1 and 2.8 μg at the cold and thermal neutron beam, respectively. The trace determination capability was examined by analyzing H in Zr and zircaloxy. By measuring 0.3 g of zirconium hydride (H content: 1.9 %) for 1000 s at the cold neutron beam, the H content was determined to be 1.6 %. The detection limit of H in 0.12 g of reactor material zircaloxy-2 (JAERI-Z1) which was measured for 10000 s at the cold neutron beam, was estimated as 8.4 ppm.

The analytical sensitivity of Hf at the cold and thermal neutron beams are 863 and 544 times higher, respectively, than that of Zr. Therefore, the present system can also be used for trace determination of Hf in Zr, which is generally difficult due to their similar chemical properties. The analytical result of Hf which was determined using the decay γ-ray at 214 keV of 179m1Hf in the above mentioned zirconium hydride was 2.0 %, with the detection limit being 58 ppm. The allowable level of Hf in reactor grade Zr is 100 ppm, therefore this system is useful for this purpose.

The system is also useful for trace determination of Cd and Hg in environmental samples. Apart from trace determination of sensitive elements, the system is also applicable to the determination of major and minor constituent element such as S, P, N, and Si in various samples. The analysis can be carried out non destructively, thus samples that cannot be dissolved or destroyed can be analyzed. Furthermore, this technique is a multi-elemental analytical method. With all these advantages this system can be applied to various types of samples in various fields such as environmental science, material science, geology, archeology, biology, and so on.

Isotopic analysis

Since γ-rays from various nuclear transition are detected, PGA can be used for isotopic analysis. The isotopic analysis of Ni and Si which is difficult to perform by mass spectrometer has been examined. Nickel consists of 5 stable isotopes of 58Ni, 60Ni, 61Ni, 62Ni and 64Ni. Compton suppression prompt γ-ray spectra of natural isotopic composition of Ni and 58Ni enriched (99.66 % enrichment) isotope are shown in Fig.1 Prompt γ-ray lines of Ni in the spectrum could be assigned by measuring enriched isotopes of 58Ni, 60Ni, 61Ni, 62Ni and 64Ni. Isotopic analysis of 28Si, 29Si and 30Si were also examined by the PGA. Usefulness of PGA for isotopic analysis has been demonstrated from the experiments.

ACKNOWLEDGMENT

The authors wish to acknowledge members of the department of research reactor of JAERI for their encouragement and Prof. R.E.Jervis for reading the manuscript.
Fig. 1 Prompt $\gamma$-ray Compton suppression spectra of $^{58}$Ni and natural Ni

REFERENCES

Utilization of Thymine Analogue as a Boron Carrier for Neutron Capture Therapy


1Department of Neurosurgery, Faculty of Medicine, Kyoto University
2Department of Chemistry, Faculty of Science, Tohoku University
3Division of Medicinal Chemistry and Pharmacology, Ohio State University
4BNCT Facility of Research Reactor Institute, Kyoto University (KUR)

ABSTRACT

The BNCT effect of 5'-carboranyl uridine (5'-CU), one of the most powerful candidate of thymine analogues as a boron carrier, was investigated on experimental brain tumor models. 5'-CU was highly accumulated into tumor cells through its multi-affinity potential to a variety of subcellular fractions of DNA/RNA and proteins. The boron concentration in tumor was more than 100 ppm, and its tumor/normal brain ratio was more than 11. Thermal neutron dose yielding 37% surviving fraction on cultured glioma cells was 3.7x10^2 nvt which was lower than that of control dose of 5.8x10^2 nvt. However, autoradiogram revealed that 5'-CU tightly binded to a variety of normal brain structures; chioloid plexus, ependymal layer and so on. Indeed, the mean surviving fraction of brain tumor rats after BNCT using 5'-CU was slightly lower than that of control rats which did not received neutrons and 5'-CU. Furthermore its cytotoxicity was not low enough, 1/10-1/20 dose of rat LD50 was required as a therapeutic dose. We are now under investigation of its clinical applicability as a boron carrier through its chemical modification in order to circumvent those problems, or warrant of further experiments in this area.

INTRODUCTION

In order to improve the BNCT effect and expand the applicable neoplasms, many boron carriers have been investigated in the bio-medical areas, i.e. amino acid analogues, porphyrine analogues, boronated monoclonal antibody (MoAb) and so on. Many carriers have been designed utilizing metabolic specificity of tumor cells and/or specific permeability of blood brain barrier. However, its tumor specificity are generally spoilt by chemical modifications of boronation. This situation is eminent in the case of MoAb. In the current BNCT, boro-captate is a useful compound due to its less cytotoxicity and easily clinical use. However, its concentration in tumor is less than 28 ppm which is theoretically minimum requirement, and also its selective binding mechanism on tumor cells has remained unclear. So that more effective compounds must be developed for further clinical purpose. In this paper, the applicability of thymine analogue as a boron carrier seeking DNA is discussed. Theoretically, maximum therapeutic gain must be obtained in this therapy, when 10^6B(n,c) 7Li reactions occurred mainly in the nucleus of the tumor cells1). Nucleic acid precursor might be suitable for
this purpose\textsuperscript{2,3}. The BNCT effect and the applicability of 5'-CU which is a thymine analogue combined with a cluster of 10 boron atoms at its 5'-position are presented here.

MATERIALS AND METHODS

The uptake of carboranyl uridine

9L gliosarcoma cells induced by a carcinogenetic ethylnitrosourea (ENU) and human glioma cells which were surprised by Japanese Cancer Research Resources Bank (JCRB) were suspended in the Dulbecco's modified Eagle medium containing 10\% fetal bovine serum. 5'-CU shown in Fig.1 was dissolved in a 2\% \(\beta\)-cyclodextrin solution and was added at various concentration into the medium. The tumor cells were incubated in the medium at 37\(^\circ\)C humidified atmosphere for 16hours containing 5\% carbon dioxide. After 5'-CU loading, the cells were washed in three times and were contained with minimum amount of essential medium in Teflon tubes for \(^{10}\)B quantitative assay by prompt \(\gamma\)-ray spectroscopy. Fractional boron concentration was also measured by same way. The cellular fractions of DNA, RNA, and protein were simply prepared by Schneider\textsuperscript{1} method.

Boron-10 distribution in tissue was determined by the \(\alpha\)-etch technique. The brain tumor rat, 14 days after implantation of 9L cells of c.a.\(10^5/10\mu l\), were used for experimental brain tumor model. 16hrs after intraperitoneal injection of 15mg 5'-CU/1.5ml 2\% \(\beta\)-cyclodextrine solution, the frozen sections of the hole brains were made.

The survival study

The cells were incubated in the same manners just mentioned above on a boron concentration of 20ppm. After loading of 5'-CU, the cells were washed in three times, and 4\(\times\)10\(^5\)cells were put into the Teflon tubes in the cylindrical shape of 1cm in diameter and 3cm high containing 1.5ml medium for thermal neutron exposure. The cells were irradiated with various dose of thermal neutrons at room temperature. The dose rate for each tubes was constant, ca.9\(\times\)10\(^9\)n/cm\(^2\)sec. After irradiation, the colony formation for surviving assay was performed for 10days. As a control study, the uptake and the BNCT effect of BSH (supplied by Boron Biologics Inc., NC, USA) were investigated in the same manners just mentioned above.

RESULTS

Boron concentration in the tumor cells were shown in Fig.2 as a function of boron concentration in medium. 5'-CU was highly accumulated into tumor cells upto ca.100 ppm as almost 10 times as BSH. Rapid increase in boron concentration suggested the passive uptake of 5'-CU into tumor cells. In the case of BSH, however, its tumor concentration slowly increased according with its concentration in medium. The fractional boron concentration revealed the strong affinity of 5'-CU to nucleic acid synthesis (Fig.3). 5'-CU might be utilized as a precursor of DNA and also RNA. This property yielded high concentration and uniform microdistribution of boron in tumor as shown in the \(\alpha\)-auto radiogram (Fig.4). However, not negligible uptake of 5'-CU into normal brain structures after intraperitoneal injection into 9L-tumor rats was revealed through this radiograms. High \(\alpha\)-signals in choroid plexus and ependymal layer were particularly observed, and those signals did not disappeared even on irrigated brain tissue. Boron concentration ratio between tumor and normal brain calculated from \(\alpha\)-plt density was ca. 11.2, which was higher than 8.1 of BSH. The survival study on
9L rat brain tumor models revealed that the mean surviving time after BNCT was slightly lower than that of control group which was not acquired with any treatments.

The retention of 5'-CU in tumor cells was acceptable for this therapy. Fig.5 shows the boron concentration in tumor as a function of incubation period in boron-free medium after 30hrs incubation loading 5'-CU. 5'-CU was retained in tumor cells for more than 20hrs.

Fig.6 shows the surviving fraction on tumor cell. 37% survival dose were 3.78X10^{12} nvt with 5'-CU and 5.80X10^{12} nvt without 5'-CU, respectively. Also the surviving fraction was larger than that of BSH. If 5'-CU was synthesized in 10B-enriched form in stead of natural boron, 10B concentration in tumor cells should increase in several times and more strong killing effect might be obtained.

DISCUSSIONS

5'-CU was highly and uniformly accumulated into tumor. It has a metabolic affinity not only to DNA but also RNA synthesis as their component material. On the other hand 2'-CU did not have selective tumor affinity due to its structural disturbance for its phosphorilation. 5'-CU was expected to be utilized as uridine for RNA component. After converted to thymine through a domestic pass way of nucleic acid in tumor cells, 5'-CU might be utilized as thymine for DNA synthesis. α-auto radiogram on rat brain tumor also suggested the uptake of 5'-CU into RNA molecules. If 5'-CU was accumulated only to DNA molecule like a similar agent of BrU, the distribution in tissue might not be uniform because more than 90% tumor cells were in the resting state which was off-state of DNA synthesis. The main reason of this affinity to RNA synthesis of 5'-CU was supposed that 5'-CU was synthesized in a non-deoxy form. However, we have not thoroughly excluded the suspicion that 5'-CU dose not bind to DNA/RNA as their component, and dose as "non-specific" agent. The uptake of 5'-CU into normal brain structures is a major disadvantage, normal brain damage was not negligible.

Cytotoxicity of 5'-CU is not still low enough for clinical use. Our preliminary study for estimation of the rat LD50 shows ca. 360mg i.p./kg bw., and pulmonary hemorrhage frequently observed at higher dose. If 5'-CU is synthesized in 10B-enriched form, 1/10-1/20 dose of LD50 might be required for clinical use. This dose is not unacceptable for cancer therapy, however, the fine chemical tuning for this agent must be employed to reduce the uptake into normal brain and also its cytotoxicity. Alternatively, repeated low dose loading might be clinically useful in order to accumulate boron in tumor and also to avoid the troublesome of its cytotoxicity, because the retention of 5'-CU in tumor cells was long enough. Anyway clinical application in this area may be difficult without solution of 5'-CU uptake on normal brain structures and its cytotoxicity.

CONCLUSIONS

5'-CU was highly and uniformly accumulated into tumor cells. However, normal brain damage was not negligible due to its multi affinity potential to a variety of normal brain structures.

Acknowledgements: This work was supported by the grant in aid for cancer research from the Ministry of Education, Science and Culture, JAPAN(No. 03151034), the Ministry of Welfare, JAPAN and from The Kyoto University Foundation. The human glioma cells were surprised from Japan Cancer Research Resources Bank(JCRB).
REFERENCES

Fig. 1. Chemical structure of 5'-carboranyl uridine. M.W. is 386.4, boron abundance is 25.3%.

Fig. 2. Boron uptake into T98G human glioma cells as a function of boron concentration in medium.
Fig. 3. Fractional boron concentration.

Fig. 4. High resolution α-auto radiogram on 9L brain tumor bearing rat.
Fig. 5. Retention of 5'-CU in T98G human glioma cells. The tumor cells were incubated in boron-free medium after 30 hours.

Fig. 6. Surviving fractions of T98G human glioma cells. C: control, $^{10}$BA: Boric acid of $^{10}$B enriched form, $^{10}$BSH: Borocaptate of $^{10}$B enriched form.
ELECTRON-ION CORRELATION IN LIQUID TE II

*Shin’ichi TAKEDA, ‡Masanori INUI, *Shigeru TAMAKI
†Kenji MARUYAMA and ††Yoshio WASEDA

* Department of Physics
College of General Education, Kyushu University
Ropponmatsu, Fukuoka-shi, Fukuoka-ken, 810 Japan

† Department of Physics
Faculty of Science, Niigata University
Niigata-shi, Niigata-ken, 950-21 Japan

‡ Graduate School of Science and Technology
Niigata University
Niigata-shi, Niigata-ken, 950-21 Japan

‡ Institute for Advanced Materials Processing
Tohoku University
Katahira, Sendai-shi, Miyagi-ken, 980 Japan

ABSTRACT

The structure factors of liquid Te have been newly obtained at 470°C and 570°C by X-ray and neutron diffraction measurements. A remarkable and clear difference has been found between X-ray and neutron diffraction results. The ion-electron correlation function and valence electron charge distribution has been evaluated from this difference at the two different temperatures. It has two maximum values around 0.82Å and 1.69Å at 470°C just above the melting temperature, which corresponds to the distribution of the lone pair electrons and covalent bonded electrons around a central tellurium ion, while it has a maximum value around 1.1Å at 570°C.

INTRODUCTION

There has been an increasing interest in liquid Te, because of its characteristic and anomalous temperature dependence of the electronic \(^1\),\(^2\) and thermodynamic properties.\(^3\) This anomalous temperature dependence has been considered as a gradual transition from non-metallic state to metallic state in the liquid state. So far many investigations have been carried out to make clear the local structure of liquid Te.\(^4\),\(^5\),\(^6\),\(^7\),\(^8\),\(^9\)
Such gradual transition was discussed within the concept of a change in the local bonding character at microscopic level.\textsuperscript{10,11}

It is reported in the solid Te that two electrons of four $5p$ electrons contribute to the bonding to form the chain structure and the other two electrons remain the nonbonding electrons. It is interesting to see how the nonbonding or bonding electrons behave at such a metal to non-metal transition in liquid Te. Liquid metals are well-known to be a binary mixture of rigid ions and conduction electrons, giving a strongly coupled plasma. The structure of liquid metals could be explicitly described in terms of three types of correlations, viz., electron-electron, electron-ion and ion-ion pairs,\textsuperscript{12,13,14} and the three types of correlations in liquid metals can be separated by the three different measurements such as X-ray, neutron, and electron diffraction.

As is well known, neutrons are scattered by nuclei at the center of ions, while, on the other hand, X-rays are scattered by both the bound electrons of all ions and valence electrons distributed among the ions. These different scattering mechanisms yield a small, but certain difference in the observed structural data of liquid metals.\textsuperscript{15,16} An effort has been made extensively by several workers from the diffraction data\textsuperscript{15} to estimate the electron charge distribution function of the conduction electrons in liquid metals.\textsuperscript{16,17,18}

In this paper, we present the results of newly measured structural data of X-ray and neutron diffraction for liquid Te, to provide the electron charge distribution in this metallic liquid and to discuss the electron charge distribution around the Te ions.

**EXPERIMENTAL AND RESULTS**

Neutron scattering measurements for liquid Te were carried out at 470$^\circ$C and 570$^\circ$C using the two axis diffractometer of Institute of Solid State Physics, The University of Tokyo at JRR-3. The sample was sealed in a quartz tube. Reflection from the (002) planes of a pyrolytic graphite crystal was used to select a neutron beam with wavelength $\lambda=1.05\text{Å}$ from the reactor neutron spectrum and the slits $(20' \times 20')$ was used to collimate the neutron beam. After the correction of the measured intensity for absorption,\textsuperscript{19} inelastic\textsuperscript{20} and multiple scattering,\textsuperscript{21} we have the structure factor, $S_N(Q)$. The experimental uncertainty in the present experiment can be evaluated as follows. The uncertainty in the wave number, $\Delta Q/Q$, is less than 8% even in low Q region near 2.0Å$^{-1}$. The accumulated intensity counts are of the order of $5.0 \times 10^4$ around the first peak region, and the order of $2.0 \times 10^4$ in other regions, while those of the empty cell are about $0.2 \times 10^4$. The total experimental uncertainties in the neutron structure factor, $S_N(Q)$, of liquid Te were estimated to be less than 1.0% and then, for example, the error bars in the $S_N(Q)$'s value are of the order of 0.02 around the first peak region.

The X-ray diffraction measurements for liquid Te were carried out at the same temperatures as the neutron diffraction measurements and the diffraction data were obtained by use of Mo-K$_\alpha$ ($\lambda=0.7107\text{Å}$) radiation. The accumulated counts by the X-ray diffraction, varying from $4 \times 10^4$ at low angles to $4 \times 10^5$ at high angles, were to hold counting statistics approximately uniform. The total experimental uncertainty in the structure factor of liquid Te does not exceed 1.0%. This follows from a detailed
Fig. 1a. Structure factors of liquid Te by X-ray (solid curve) and neutron diffraction (closed circle) at 470°C, and difference between two curves, \([S_X(Q) - S_N(Q)]\), for liquid Te.

Fig. 1b. Structure factors of liquid Te by X-ray (solid curve) and neutron diffraction (closed circle) at 570°C, and difference between two curves, \([S_X(Q) - S_N(Q)]\), for liquid Te.
discussion of the source of systematic errors in the X-ray diffraction experiments. Thus the uncertainty is the order of 0.02 in the value of $S_X(Q)$ near the first peak region. In both case, $S(Q \to 0)$ is determined by the thermodynamic measurements of density and sound velocity and specific heat.

Figures 1a and 1b show the structure factors of liquid Te at 470°C and 570°C determined by neutron and X-ray diffraction. The systematic differences are well appreciated, although the qualitative coincidence in the structural profile is almost retained. The quantity of $[S_X(Q) - S_N(Q)]$ evaluated from two structure factors is also given in the bottom of Figs. 1a and 1b, which may be a help to see the well appreciated systematic difference and oscillating profile in $[S_X(Q) - S_N(Q)]$.

**ANALYSIS**

The essential points of the method for evaluating the electron-ion correlation in liquid metals are given below and the details are described elsewhere. If we use the Ashcroft-Langreth type partial structure factors of a binary mixture composed of ions(i) and electrons(e), the total X-ray scattering intensity except for $Q = 0$ is expressed as follows;

$$I_X(Q)/N = [f^2_i(Q)S_{ii}(Q) + 2\sqrt{Z}f_i(Q)S_{ie}(Q) + zS_{ee}(Q)] + (Z - z)S_{inc}^{inc}(Q),$$

where $f_i(Q)$ is the form factor of the ion, $Z$ the atomic number and $z$ the number of valence electrons per atom. $S_{ii}(Q)$, $S_{ie}(Q)$ and $S_{ee}(Q)$ are the partial structure factors of ion-ion, ion-electron and electron-electron pairs, respectively and $S_{inc}^{inc}(Q)$ is the incoherent (Compton) scattering factor of ions. Hence we can obtain the coherent X-ray scattering intensity, $I_X^{coh}$, which can be determined from measured intensity data, and it can be properly approximated as following form, except for very light elements such as Li and Be.

$$I_X^{coh}(Q) = [f_i(Q) + \rho(Q)]^2S_{ii}(Q)$$

$$\approx f_i(Q)^2S_{ii}(Q) + 2\sqrt{Z}f_i(Q)S_{ie}(Q).$$

The partial structure factor for ion-ion pairs is equal to the coherent structure factor determined by neutron diffraction, $S_{ii}(Q) = S_N(Q) = I_N^{coh}(Q)/Nb^2$, where $b$ is the scattering length of neutrons and $I_N^{coh}(Q)$ is the coherent neutron scattering intensity. Therefore, the electron-ion correlation, $S_{ie}(Q)$, and the valence electron charge distribution in the momentum space, $\rho(Q)$, and both relation can be given by

$$S_{ie}(Q) = \frac{1}{2\sqrt{Z}f_i(Q)}[I_X^{coh}(Q) - f_i^2(Q)S_N(Q)].$$

$$\rho(Q) = [b^2I_X^{coh}(Q)/I_N^{coh}(Q) - f_i(Q)^2]/2f_i(Q)$$

$$= \sqrt{Z}S_{ie}(Q)/S_{ii}(Q) = \sqrt{Z}S_{ie}(Q)/S_N(Q).$$
Fig. 2. Ion-electron structure factor in liquid Te.

\[ S_{ie}(Q) = [\rho(Q)/\sqrt{z}]S_{ii}(Q). \]  

(5)

The ionic form factor for Te$^{4+}$, \( f_i(Q) \), is calculated by Hartree-Fock method, and it can also be obtainable from the X-ray scattering intensity measurements for the ionic crystals. Eqs. (3) and (4) enable us to evaluate the partial structure factor of ion-electron pairs \( S_{ie}(Q) \) from measured structural information of \( S_X(Q) \) and \( S_N(Q) \).

The partial pair correlation function between ions and electrons, \( g_{ie}(r) \), and charge density around a Te$^{4+}$ ion, \( \rho(r) \), can be obtained from \( S_{ie}(Q) \) and \( \rho(Q) \) by the Fourier transformation,

\[ g_{ie}(r) = 1 + \frac{1}{2\pi^2 \rho_0 r} \int_0^\infty \sqrt{z} S_{ie}(Q) Q \sin Qr \, dQ, \]  

(6)

\[ \rho(r) = \frac{1}{2\pi^2 \rho_0 r} \int_0^\infty \rho(q) \sin Qr \, dQ, \]  

(7)

where \( \rho_0 = zN/V_M \) and \( V_M \) being the molar volume and \( N \) the Avogadro’s number.

**DISCUSSION**

The partial structure factor of ion-electron pairs, \( S_{ie}(Q) \), for liquid Te is evaluated from Eq.(3) and the result at 470°C is given in Fig.2. The vertical lines in this figure indicate the experimental uncertainty due to the statistical counting error of the X-ray and neutron diffraction measurements. The information on \( S_{ie}(Q) \) presently obtained
Fig. 3.  Partial pair correlation function in liquid Te at 470°C (dotted curve) and 570°C (solid curve).

is enough to discuss the partial pair correlation functions, although the information $S_{ie}(Q)$ is limited to $Q_{\max} = 8.7 \text{Å}^{-1}$.

The partial pair correlation functions for ions and electrons, $g_{ie}(r)$, are obtained from the corresponding $S_{ie}(Q)$ at 570°C and shown in Fig.3. The charge distribution around a Te ion, $4\pi r^2 \rho_0 g_{ie}(r)$, is obtained from $g_{ie}(r)$, and $4\pi r^2 \rho_0 g_{ie}(r)$ has the first peak at 0.82 Å and the second one around 1.69 Å at 470°C. According to the theoretical study of crystalline Te by Joannopoulos, the charge density maxima of two non-bonding p-electrons (lone pair) and of two bonding p-electrons (σ-bond) around a central atom are located at distances of 0.85 Å and 1.45 Å, respectively. Hence the first peak in $g_{ie}(r)$ at 470°C corresponds to the charge distribution of the lone pair electrons around the Te$^{4+}$ ion and the second peak shows the electron charge distribution of the bonding state in liquid Te.

On the other hand, at 570°C, the partial pair correlation function, $g_{ie}(r)$, seems quite different from that at 470°C. It has a broad and distinct peak around 1.0 Å. This behaviour of charge distribution is quite similar to the case of simple liquid metals as liquid Al. This suggests the characteristic property of conduction electrons to come to screen the ionic potential of Te$^{4+}$. This metallic property may hold for the charge of 5p-electrons in liquid Te at 570°C.

To see the electron configuration around an ion more clearly, it may be useful to deduce the electron charge density distribution, $\rho(r)$, in real space around a central ion. The electron charge distribution, $\rho(r)$, can be obtained from the charge density distribution in $Q$ space, $\rho(Q)$, or from the electron-ion correlation function $S_{ie}(Q)$. The resultant $\rho(r)$'s are shown in Fig.4. The dotted and solid curves in the figure represent
Fig. 4. Valence electron charge distribution around the Te ion in liquid Te in real space. (dotted curve: at 470°C, solid curve: at 570°C). That of an isolated Te ion is denoted by a chain curve.

the charge density distribution at 470°C and 570°C, respectively. As seen in the figure, the curve of real electron distribution, $4\pi r^2 \rho(r)$, has a maximum value around 0.82Å and 1.69Å at 470°C and the coordination numbers are 0.7 and 3.3, respectively.

Liquid Te has an anomalous temperature dependence of electrical conductivity and this anomaly has been considered as a gradual transition from a non-metallic state to a metallic one. The transition is related to the change of the local bonding character from two fold to three fold coordination. Above results show that liquid Te is composed of about 35% twofold and 65% three fold coordinated atoms just above the melting temperature, and this is consistent with the results obtained from the specific heat.

Since the ordinary ion-ion radial distribution function of liquid Te near the melting temperature obtained by neutron diffraction shows 2.7 ions within a distance of 2.90Å as the nearest neighbour ions, this is also consistent with our results. If the three electrons among four 5p electrons form bonding orbitals, one electron must occupy an anti-bonding orbital. This may cause the bonding distance to be stretched to some extent in the liquid state compared with the solid state and, as a result, liquid Te may have metallic properties.

On the other hand, the curve of $4\pi r^2 \rho(r)$ has a maximum around 1.05Å and a small hump around 2.15Å at 570°C, and the coordination number around first peak region is about 3.0. The profile of the charge density distribution around a Te ion at 570°C becomes quite similar to the case as simple metallic one.

In conclusion, we have obtained the fundamental information on the valence electron charge distribution in liquid Te just above the melting temperature, at 470°C, and at 570°C, corresponding to the change from non-metallic to metallic state in liquid Te.
ACKNOWLEDGEMENTS

The authors are grateful to Professor A. Azuma for providing the wave-function of an isolated Te ion. The authors are also grateful to the Ministry of Education, Science and Culture of Japan for financial support of Grant-in-Aid. Two of the authors (M.Inui and S.Takeda) are grateful to the Japan Science Society for financial support of Grant-in-Aid. The authors are grateful to The Institute of Solid State Physics, The University of Tokyo, for providing us facilities to use the diffractometer 4G in JRR-3.

REFERENCES

GADOLINIUM NEUTRON CAPTURE THERAPY: PRECLINICAL STUDIES

Yasuyuki AKINE, Nobuhiko TOKITA*, Koichi TOKUYUE, Michinao SATOH and Hisahiko CHUREI

The National Cancer Center Hospital
5-1-1 Tsukiji, Chuou-ku, Tokyo, 104 Japan
*Visiting researcher

ABSTRACT

Gadolinium neutron capture therapy makes use of photons and electrons produced by nuclear reactions between gadolinium and lower-energy neutrons which occur within the tumor. The results of our studies have shown that its radiation effect is mostly of low LET and that the electrons are the significant component in the over-all dose. The dose from gadolinium neutron capture reactions does not seem to increase in proportion to the gadolinium concentration, and the Gd-157 concentration of about 100 µg/ml appears most optimal for therapy. Close contact between gadolinium and the cell is not necessarily required for cell inactivation, however, the effect of electrons released from intracellular gadolinium may be significant. Experimental studies on tumor-bearing mice and rabbits have shown that this is a very promising modality though further improvements in gadolinium delivery to tumors are needed.

INTRODUCTION

Neutron capture therapy is based on nuclear reactions between low-energy neutrons and an element having a high probability of interacting with them. In 1936 Locher postulated neutron capture therapy with several elements\(^1\). During the 1950'–1960s this proposal became realized at the Brookhaven National Laboratory in New York where the first clinical trial with boron took place\(^2\). Renewed interest in this modality emerged recently when a 5-year survival rate of 20% was achieved in patients with grades III-IV gliomas treated with boron neutron capture therapy \(^3\).

Gadolinium, a rare earth element with a strong paramagnetic property, has been widely used as a contrast-enhancing element in magnetic resonance imaging (MRI) in the form of
meglumine gadopentetate (MG). Among its several isotopes, Gd-157 has a very large nuclear cross section to thermal neutrons (67 times larger than that of B-10), and releases photons and electrons with the maximal energy of 7.9 MeV when bombarded with thermal neutrons\(^4\). Thus, a half a century after Locher suggested\(^1\) investigation begun on Gd-157 as an agent for neutron capture therapy. In this report, we review the results of our preclinical studies to evaluate the feasibilities of gadolinium neutron capture therapy (GNCT) as a potential clinical modality.

**IN VITRO STUDIES**

These studies were carried out to evaluate the extent and quality of radiation effects caused by gadolinium neutron capture reactions (GNCR) using standard cell survival assays. Attempts have been made to develop a formula to estimate doses resulting from GNCR.

**Dose response studies**

The first study was aimed at obtaining a cell survival curve to measure dose responses and to speculate the quality of radiations released from GNCR. Chinese hamster (V79) cells in suspensions were placed in Teflon tubes (6 cm long, 0.8 cm in outer diameter) containing medium and 5,000 μg/ml gadolinium (783 μg/ml Gd-157) in the form of meglumine gadopentetate (MG; Magnevist, Schering AG, Berlin, Germany), and were exposed to thermal neutrons generated by a TRIGA II reactor at the Musashi Institute of Technology. Measured dose rates with TLD were 1.05 Gy/h for a Teflon tube filled with 1.7 ml of water; and 10.0 Gy/h for the one filled with 1.7 ml of water containing 783 μg/ml Gd-157. There was a 35% depression of the thermal neutron fluence across the Teflon tube. Cells were plated in petri dishes and colonies were counted after 7 days.

The results show that the survival curve was found to be simple exponential for cells exposed to thermal neutrons only. The survival curve for cells irradiated in the presence of gadolinium exhibited a shoulder at the low neutron fluence region, and when fitted with a linear-quadratic model, the α/β ratio was 2.17, suggesting that the radiation effect is mainly of low LET. The contribution of neutrons was found to be very small when compared to photons and electrons, though this depends largely on the gadolinium concentration. The enhancement of thermal neutron effects by gadolinium, therefore, was 3.6 fold when measured at 10% survival levels\(^5\).

**Electron contributions**

The second study was to assess contributions of each radiation component of GNCR to the total dose. The survival data described above were plotted based on the available dosimetry data which consisted of doses (in Gy) from neutrons, gamma rays from both GNCR and the reactor core, excluding electrons. For comparison, an x-ray survival curve, derived from 6 separate experiments, was obtained using 250 KVP x-rays (General Electric Maxitron, 2 mm
Cu HVL) at a dose rate of 1.2-1.4 Gy/min.

When the two survival curves were plotted as a function of dose (Gy), there was a significant difference in the 10% survival dose: 1.9 Gy for cells received GNCT and 9.1 Gy for cells irradiated with x rays. Thus, the difference of 7.2 Gy must have come from the electrons. The results indicated that the electrons were the significant component of the radiation effect caused by GNCR.

Biological dosimetry

The third study employed biological dosimetry to estimate the dose from GNCR since physical dosimetry has not been established for the electron component. To accomplish this, several survival curves were generated after cells suspended in medium containing MG (0 to 3132 μg/ml Gd-157) were exposed to thermal neutrons at the Heavy Water Facility of the Kyoto University Reactor (KUR, 5MW, 3x10^8 thermal neutrons/cm²/sec.; a gamma dose rate of 1 Gy/hr). For comparison, the x-ray survival curve as described above was used (Fig. 1a). The survival curves for cells irradiated in the presence of gadolinium exhibited a shoulder at the low-neutron fluence region, therefore, they were fit with a linear-quadratic model. The neutron fluence for any given survival level was calculated accordingly (Fig. 1b).

![Fig.1 (a)](image1.png)

![Fig.1 (b)](image2.png)

**Fig.1 (a)** Survival of cells exposed to 250 KVP x rays. **(b)** Survival curves for cells suspended in MG (0-3132 μg/ml Gd-157) and exposed to thermal neutrons. Note the presence of shoulders on the survival curves except for the one with 0 μg/ml Gd-157 (neutrons only).

Based on the results, x-ray equivalent doses for any effects resulting from GNCR can be estimated by matching the survival levels. For example, if GNCR given under a condition resulted in 10% survival, this survival level corresponds to 9.1 Gy with x rays, hence, the dose from the GNCR was equivalent to 9.1 Gy x rays. After analyzing the survival curves, an x-ray equivalent dose has been tentatively estimated as: Deq (Gy) = 0.56 N1.36Gm, where m
\[ 0.407N - 0.267; \] Deq is the x-ray equivalent dose in Gy; \( N \), the value obtained by neutron fluence /10^{12}/cm^{2}; and \( G \), the Gd-157 concentration (\( \mu g/ml \))\(^7\). The equation provides only approximate values and is valid within the data ranges shown in Fig. 1b.

To evaluate the extent of MG enhancement of the thermal neutron effect, the thermal neutron fluence required for the 10% survival was plotted as a function of Gd-157 concentration. The results showed that the required fluence decreases rapidly between 0 to about 100 \( \mu g/ml \) Gd-157, indicating a high rate of enhancement of the thermal neutron effect in this region\(^7\).

**IN VIVO STUDIES**

Three separate studies, two with mouse subcutaneous and ascites tumor models, and one with rabbit tumors, have been carried out to evaluate the efficacy of different methods of gadolinium delivery to tumors.

**Subcutaneous tumors in mice**

The first study was aimed at evaluating (1) the dynamics of MG given subcutaneously in mice; (2) the response of tumors after GNCT, and (3) estimation of the tumor dose.

Three-week-old ICR male mice were inoculated with Ehrlich ascites tumor cells (3 x 10^6 cells/0.1 ml PBS) with 0.1 ml PBS or 0.1 ml MG (37.1 mg) at one or two subcutaneous sites on the dorsum. The mice were then individually exposed to thermal neutrons (~1.1 x 10^{12} neutrons cm^{-2}) at KUR for 8 minutes. The biological endpoint was the time period required for mice to form tumors with an arbitrary size of 100 mm^{2} (a product of two perpendicular axes). In a separate study three groups (n = 10 each) were similarly inoculated and irradiated with 3 MeV electrons receiving a total dose of 5, 12 or 20 Gy at a dose rate of approximately 2 Gy/min.

The dynamics of MG after subcutaneous injection, measured with Gd-153-MG (0.5 mmol MG/50\( \mu \)Ci/ml) by radioactivity counting, revealed that the residual MG concentration at the inoculation site was reduced to 78\% (4.7 mg Gd-157/ml) at the beginning and 61\% (3.6 mg Gd-157/ml) at the completion of neutron irradiation.

The tumor responses showed that it took 28.7 ± 2.3 days for mice treated with neutrons and MG (N+, Gd+) to form 100 mm^{2} tumors; 15.2 ± 0.2 days for those treated with neutrons without MG (N+, Gd-); and 7.3 ± 0.4 days for those unirradiated with (N-, Gd+) or without (N-, Gd-) MG.

Time periods required for mice irradiated 5, 12 or 20 Gy to form 100 mm^{2} tumors were 10.9 ± 2.4, 21.4 ± 5.4, and 35.0 ± 7.1 days, respectively. Thus, the corresponding electron doses for groups (N+, Gd-) and (N+, Gd+) are 7.8 and 16.2 Gy, respectively, and a 2.1 fold (16.2/7.8) enhancement was obtained by the presence of MG\(^8\).

**MG-containing microcapsules in murine ascites tumors**
The second study was to evaluate MG-containing microcapsules as a gadolinium carrier. The microcapsules (MG content 31% W/W) release MG slowly (14% of the total MG released in 20 min) when suspended in saline9). ICR mice were anesthetized and inoculated intraperitoneally (ip) with 10⁷ Ehrlich ascites cells in 0.2 ml PBS. MG or placebo microcapsules (220 mg) were suspended in 0.5 ml dextran 40 just before use and were administered ip. The mice were individually exposed to \(2.16 \times 10^{12}\) thermal neutrons cm\(^{-2}\) at KUR. Nine mice received MG microcapsules and neutron irradiation (Gd+, N+), and ten were given placebo microcapsules and neutron irradiation (Gd-, N+). Control consisted of two groups of 14 mice each receiving 10⁷ tumor cells and MG (Gd+, N-), or placebo (Gd-, N-) microcapsules without neutron irradiation.

The results show that mice given MG microcapsules survived significantly longer than those given placebo microcapsules or control at 60 days (p<0.05) with two of the nine mice surviving without disease at 180 days. All mice in other groups died within 17 days after treatments a result of progressive accumulation of tumor cells. None of the mice given MG or placebo microcapsules and neutron irradiation showed any sign of intestinal injury such as diarrhea. The estimated Gd-157 concentration in microcapsules was 2.5 mg/ml peritoneal fluid, and the dissolved Gd-157 in the peritoneal fluid was estimated to be 370 μg/ml or less. At this concentration and the neutron fluence given, the radiation effect from the extramicrocapsular Gd-157 dissolved in the peritoneal fluid was expected to result in in 20% survival levels. Hence, the cytotoxic effect on the ascites tumor cells was mainly due to radiations produced from MG in the microcapsules rather than those from dissolved MG. The results show that microcapsules improved both the Gd-157 retention periods and survival10).

Intraarterial infusion of MG to rabbit tumors

The third study was aimed at examining the efficacy of gadolinium delivery to tumors by intraarterial infusion. Four New Zealand White rabbits (10-20-week-old male weighing 2.3-3.1kg) bearing VX-2 tumors in both hind legs were used for GNCT, and two for gadolinium concentration studies. During neutron irradiation MG was infused through a catheter preinserted into a branch of the left femoral artery at a flow rate of 0.48 ml/min. Under general anesthesia the rabbits were exposed individually to KUR thermal neutrons for 40 min while a total volume of 19 ml of MG fluid (334 mg MG) had been infused. The average neutron fluence measured was \(2.1 \pm 0.47\) x 10¹² neutrons cm\(^{-2}\) s\(^{-1}\), and the photon dose was 4.4 ± 3.1 Gy for gadolinium-infused legs, and 3.7 ± 1.1 Gy for control legs. Gadolinium concentrations in the tumor and the surrounding normal tissue 11) after infusing MG for ten minutes (0.48 ml/min) were 1.55 μmol/g (2.32 and 0.774 ) for the tumors, and 3.56 μmol/g (5.48 and 1.62) for the adjacent normal tissue of the MG-infused legs; 0.29 μmol/g (0.40 and 0.17) for the tumors, and 0.17 μmol/g (0.25 and 0.09) for the normal tissue of the contralateral legs.

The results revealed that the average tumor size of the infused legs was smaller than that of the contralateral legs with a statistically significant difference (p < 0.05) from the 16th day to
the end of observation (the 23rd day)\textsuperscript{12}. There were no changes noted macroscopically or histologically in any of the normal tissue samples reviewed. No selective gadolinium delivery to tumors has been achieved with this approach; however, the obtained Gd-157 concentration in the tumor was approximately 40 - 90 \( \mu \text{g/ml} \) which was high enough for neutron capture therapy\textsuperscript{7}.

**DISCUSSION AND CONCLUSIONS**

The *in vitro* studies have shown that the radiation effect resulting from GNCR is mostly of low LET which differs itself from boron neutron capture therapy where released radiations are of high-LET particles. The dose distributions of released photons alone in GNCT are reported to be comparable to those obtained in BNCT\textsuperscript{13,14}. Considering the broad energy range of released electrons, and that Auger, and other low-energy electrons are known to have a very limited range in tissue and are of high LET\textsuperscript{15}, the location of gadolinium in the cell, particularly with respect to cellular DNA is crucial in determining the degree of biological effects inflicted upon by GNCR. This has been shown by studies which revealed that double strand breaks caused by neutron irradiation were enhanced in the presence of gadolinium and that the effects were markedly reduced when gadolinium was sequestered from the nucleus\textsuperscript{16}. Our preliminary study indicates that MG enters both human and animal cells freely (Akine et al, unpublished data 1993) which suggests that the contribution of low-energy electrons may be significant. Recently, contributions of electrons and photons have been estimated by Monte Carlo calculations\textsuperscript{17}.

For GNCT to be effective, it is important to maintain gadolinium concentrations in the surrounding normal tissue as low as possible. The *in vivo* studies have shown no adverse effect on normal tissue while there has been significant tumor growth suppression. It is still premature to determine the extent of normal tissue damage after GNCT. We are presently looking into other gadolinium carriers such as porphyrin-gadolinium complex. As a delivery system, we are investigating transcatheter arterial embolization as well as direct intratumoral administration.

In the future, other developments are needed in nuclear engineering to provide epithermal rather than thermal neutrons so that deep-seated tumors can be treated. Furthermore, to make neutron capture therapy practical, it is desirable to develop a hospital-based slow-neutron accelerator. In conclusion, the results are still preliminary but very encouraging enough to justify further investigation of this modality.

**ACKNOWLEDGEMENTS**

This work was supported in part by Grant-in-Aid for Cancer Research (4-13) from the Japanese Ministry of Health and Welfare; Grant-in-Aid for Science Research (Special Research on Cancer [1] 03151034) from the Japanese Ministry of Education, Science and
Culture; and the Visiting Researchers' Program of the Research Reactor Institute, Kyoto University. We thank Dr. H. Tanooka for his support on this project. A part of meglumine gadopentetate and gadolinium measurements were provided by Schering Japan.

REFERENCES

1) Locher GL. Biological effects and therapeutic possibilities of neutrons. AJR 36: 1-13, 1936
11) Nomura S and Azuma H. The quantitative determination of Gd-DTPA in biological


15) Burki HJ, Roots R, Feinendegen LE and Bond VP. Inactivation of mammalian cells after disintegration of $^3$H or $^{125}$I in cell DNA at -196 C. Int J Radiat Biol 23: 363-375, 1973


GROWTH INHIBITION OF HUMAN PANCREATIC CANCER GRAFTS IN NUDE MICE BY BORON NEUTRON CAPTURE THERAPY

H. Yanagië¹, Y. Fujii¹, K. Kosaki¹, Y. Saegusa¹, T. Tomita², M. Sekiguchi¹* and H. Kobayashi³.

¹Department of Clinical Oncology, ²Laboratory for Culture Collection, Institute of Medical Science, University of Tokyo, 4-6-1 Shiroganedai, Minato-ku, Tokyo 108, Japan
³Institute of Atomic Energy, Rikkyo University, 2-5-1 Nagasaka, Yokosuka 240-01, Japan
*Present address: Department of Surgery I, Saitama Medical School, Moroyama-chou, Iruma-gun, Saitama 350-04

ABSTRACT

Cell destruction in boron neutron capture therapy (BNCT) is due to the nuclear reaction between $^{10}$B and thermal neutrons to release alpha-particles (⁴He) and lithium-7 ions (⁷Li). The ⁴He kills cells in the range of 10 μm from the site of ⁴He generation. Therefore, it is theoretically possible to kill tumor cells without affecting adjacent healthy tissues, if $^{10}$B-compounds could be selectively delivered. We have described that $^{10}$B atoms delivered by immunoliposomes exerted cytotoxic effect on human pancreatic carcinoma cells (AsPC-1) in a dose-dependent manner by thermal neutron irradiation in vitro as reported previously.

In the present study, the cytotoxic effect of a locally injected $^{10}$B compound solution or multilamellar liposomes containing a $^{10}$B compound to human pancreatic carcinoma xenograft in nude mice was evaluated after thermal neutron irradiation. AsPC-1 cells (1 x $10^7$) injected subcutaneously into a nude mouse grew to a tumor weighing 100-300 mg after 2 weeks. At this time 200 μg $^{10}$B compound was locally injected in the tumor and irradiated with 2 x $10^{12}$ n/cm² thermal neutron.

Tumor growth of $^{10}$B-treated groups was suppressed as compared with control group. Histopathologically, hyalinization and necrosis were found in the tumor tissues. For effective tumor destruction, $^{10}$B dose more than 60 μg was necessary. The tumor tissue injected with saline only and irradiated showed neither destruction nor necrosis.

These data indicate that the accumulation of $^{10}$B atoms to the tumor site is mandatory for the cytotoxic effect by thermal neutron irradiation.
INTRODUCTION

Cytotoxic effect of boron neutron capture therapy (BNCT) is due to the nuclear reaction between $^{10}$B and thermal neutrons. This nuclear reactions as followed:

$$^{10}\text{B} + \text{1n} \rightarrow ^{4}\text{He} + ^{7}\text{Li} + 2.4 \text{ MeV}$$

The produced $^4\text{He}$ killed cells in the range of 10μm from the site of the capture reaction\(^1,2\)). Therefore, it is theoretically possible to kill the tumor cells without affecting the adjacent normal cells, if efficient $^{10}\text{B}$ atoms could be selectively accumulated in the tumor cells. BNCT has been applied clinically for treatment of malignant brain tumors\(^3\) or malignant melanoma\(^4\).

Recently, liposomes have attracted attention as drug delivery system (DDS). It is possible to carry a large amount of $^{10}\text{B}$ compound in a liposome, and therefore, the liposome could deliver a large amount of a $^{10}\text{B}$-compound to a tumor cell. We have described that $^{10}\text{B}$ atoms delivered by immunoliposomes exerted cytotoxic effect on human pancreatic carcinoma cells (AsPC-1) in a dose-dependent manner by thermal neutron irradiation \textit{in vitro} as reported previously\(^5\).

In the present experiment, we prepared a $^{10}\text{B}$-compound solution in several concentrations and a liposome containing a $^{10}\text{B}$ compound. The intratumoral injection of $^{10}\text{B}$ solutions and boronated liposomes inhibited tumor cell growth on thermal neutron irradiation \textit{in vivo}.

MATERIALS & METHODS

Chemicals

The cesium salt of undeca hydro-mercaptoelo-sodecaborate (Cs$_{2}^{10}$B$_{12}$H$_{11}$SH) was kindly supplied by Shionogi Research Laboratories Co. Ltd. (Osaka, Japan). The solubility of the compound in water was 250 mM at 40°C.

Egg yolk phosphatidylcholine (Egg PC) was gift from Nippon Fine Chemical Co. (Osaka, Japan). Cholesterol was obtained from Sigma Chemical Co. Ltd. (St. Louis, MO, USA). Dipalmitoylphosphatidylethanolamine (DPPE) was from Calbiochen-Behring (San Diego, CA, USA).

Target Tumor cells and mice

Male BALB/c nu/nu mice were obtained from Nihon SLC (Shizuoka, Japan), and used at 6 to 7 weeks of age. Human pancreatic carcinoma cell line AsPC-1, producing carcinoembryonic antigen (CEA), was obtained from Dainihon Seiyaku Co. Ltd. (Osaka, Japan) and
maintained in RPMI 1640 medium (Hazleton Biologics, INC, Kansas, USA) supplemented with 10% fetal calf serum (Cell culture Laboratories, Ohio, USA).

Preparation of liposomes containing $^{10}$B-compound

Egg yolk PC (5 μ moles), cholesterol (5 μ moles) and DTP-DPPE (0.25 μ moles) were dissolved in chroloform-methanol (2:1) and mixed in a conical flask. The organic solvent was removed by evaporation at 40°C. A half ml of 250 mM $^{10}$B compound solution was added to the dried lipid film and then multilamellar vesicles were prepared by vortex dispersion.

Gamma-ray irradiation of cells

AsPC-1 ($5 \times 10^4$) cells were irradiated by gamma-rays from the $^{137}$Cs source in Gamma Cell 40 (Atomic Energy of Canada, Ottawa, Canada). After irradiation, 0.25 μCi $^3$H TdR was added to each well and incubated for further 8 h. Then, the cells were harvested and the incorporated thymidine was estimated in a liquid scintillation spectrometer.

Determination of gamma-ray dose generated at thermal neutron irradiation site in thermal column

The gamma-ray generated during thermal neutron irradiation was measured using the ionisation chamber method (ICRU, 1964) at the irradiation points.

Thermal neutron irradiation

AsPC-1 cells ($1 \times 10^7$) were injected subcutaneously to the back of male BALB/c nu/nu mice. About 10 - 14 days after injection, when the estimated tumor weight reached to 100 - 300 mg, 0.2 ml of each $^{10}$B solution (0, 500, 1000, 2000 ppm) or boronated liposomes were injected into the tumors. After injection, the mice were irradiated with $2 \times 10^{12}$ n/cm$^2$ thermal neutron at the TRIGA-II atomic reactor of Rikkyo University (Yokosuka, Japan). After irradiation, the effect of BNCT was evaluated on the basis of tumor weight (calculated as $1/2 \times$ length $\times$ width$^2$) and histological findings of the tumors at 3-day intervals.

RESULTS

Effect of gamma-rays generated by thermal neutrons

Cells irradiated with thermal neutrons were also irradiated with various doses of gamma-rays concomitantly generated depending on the neutron dose. $2 \times 10^{12}$ and $5 \times 10^{12}$ n/cm$^2$ of thermal neutron fluences generated 1.03 and 3.36 Gy of gamma-ray, respectively, in the thermal column of TRIGA-II atomic reactor of Rikkyo University. Less than 1.03 Gy of gamma-rays did not exert any inhibitory effect on AsPC-1 cell growth. As the growth of AsPC-1 cell was suppressed
weakly with 3.36 Gy gamma-ray, the thermal neutron fluences at less than $2 \times 10^{12}$ n/cm$^2$ were used in the present experiment.

**Growth inhibition of tumor treated with $^{10}$B solutions**

In order to examine the therapeutic effect of $^{10}$B solutions on the growth of AsPC-1 cells, the tumor-bearing mice were injected intratumorally with $^{10}$B solutions. The concentrations of $^{10}$B solutions were 0 (control, saline), 500, 1000 and 2000 ppm. After intratumoral injection of $^{10}$B solutions, the mice were irradiated with $2 \times 10^{12}$ n/cm$^2$ thermal neutron. As shown in Figure 1, inhibition of tumor growth was observed in all of the three groups treated with $^{10}$B solutions as compared with the control group. The inhibition was dose-dependent.

These results indicate that intratumoral injection of $^{10}$B solutions exerts toxic effects on AsPC-1 cells and inhibit the tumor growth in vivo upon thermal neutron irradiation.

**Pathological findings of tumor treated with $^{10}$B solutions**

The therapeutic effects of $^{10}$B solutions was noticeable from the pathological findings of tumor specimens. The surface of tumor became necrotic and the weight of tumor did not increase in all of the three groups treated with $^{10}$B solutions. However, the control group ($^{10}$B: 0 ppm) continued to grow. The necrotic portions of tumor were replaced by fibrosis and hyalinization histologically.

**Growth inhibition of tumor treated with boronated liposomes**

The effect of $^{10}$B compound entrapped in liposomes on the AsPC-1 cell growth was examined after thermal neutron irradiation. Liposomes were prepared by using 250 mM $^{10}$B compound. The amount of $^{10}$B in liposomes thus prepared was $623 \pm 80 \mu$g/ml liposome. As shown in Figure 2, intratumoral injection of liposomes prepared with 250 mM $^{10}$B compound inhibited the tumor cell growth as significantly as those prepared with 2000 ppm of $^{10}$B. The liposomes could keep $^{10}$B atoms at the tumor site, unlike the $^{10}$B compound solutions alone. These results indicate that the liposomes could carry the $^{10}$B compound to the target cells and exert the toxic effect on them.

**DISCUSSION**

We showed previously that the boronated-immunoliposome attached to AsPC-1 tumor cells and suppressed growth in vitro upon thermal neutron irradiation. The suppression was dependent upon the concentration of the $^{10}$B compound in the liposomes and on the density of antibody conjugated to the liposomes$^{51}$. In the present experiment, the intratumoral injection of $^{10}$B
solutions or boronated liposomes suppressed tumor cell growth \textit{in vivo} after thermal neutron irradiation. The surface of the tumor became necrotic and tumor size decreased. The necrotic portion was replaced by hyalinization and fibrosis in pathological findings.

The inhibition of tumor growth after injection of boronated liposomes was dependent upon the concentration of $^{10}\text{B}$ compound in the solution. A liposome had capacity for keeping the high concentration of $^{10}\text{B}$ compound in the tumor. These results suggested that liposomes containing $^{10}\text{B}$ compound could be applied in BNCT as effective carriers of $^{10}\text{B}$ compound to target cells.

Liposomes were found to be potential tool for BNCT, but many problems remain to be solved for more selective accumulation of $^{10}\text{B}$ compound to the tumor cells \textit{in vivo}. We confirmed that immunoliposomes suppressed tumor cell growth \textit{in vitro} after thermal neutron irradiation, and as the next step, we would like to apply the intratumoral injection of boronated immunoliposome to improve efficiency of targeting of $^{10}\text{B}$ to the tumor cells.

\section*{REFERENCES}

Fig. 1. Therapeutic effect of $^{10}$B compound administrated in several concentrations on the growth of AsPC-1 inoculated on the back of BALB/c nu/nu mice. The results are expressed as relative mean tumor weights ($W_1 / W_0$), where $W_1$ is the tumor weight at a given time and $W_0$ at the initiation of treatment. The tumor weight was calculated as $1/2 \times$ length $\times$ width$^2$ of the tumor. About 14 days after inoculation of AsPC-1 cells, $^{10}$B solutions (500, 1000 and 2000 ppm) or boronated liposomes, saline as control were injected into the tumors. After injection, the mice were irradiated with $2 \times 10^{12}$ n/cm$^2$ thermal neutron: 500 ppm (□□), 1000 ppm (△△), and 2000 ppm (○○)$^{10}$B solution were prepared. Saline was used as control (●●).

Fig. 2. Growth inhibition of AsPC-1 cells treated with boronated liposomes. After inoculation of AsPC-1, saline (●●), 2000 ppm $^{10}$B solution (△△) or boronated liposomes (○○) were injected into the tumors. Amount of $^{10}$B in liposomes prepared by using 250 mM $^{10}$B compound was 623 ppm (mean). After injection, the mice were irradiated with $2 \times 10^{12}$ n/cm$^2$ thermal neutron. The results were expressed as relative mean tumor weight ($W_1 / W_0$), as in Fig. 1.
PHANTOM EXPERIMENT OF DEPTH-DOSE DISTRIBUTIONS FOR GADOLINIUM NEUTRON CAPTURE THERAPY

T. Matsumoto, K. Kato and Y. Sakuma

Atomic Energy research Laboratory
Musashi Institute of Technology
Ozenji 971, Asao-ku, Kawasaki-shi
215 Japan

A. Tsuruno and M. Matsubayashi

Tokai Research Establishment, JAERI
Tokaimura, Naka-gun, Ibaraki-ken
319-11 Japan

ABSTRACT

Depth-dose distributions in a tumor simulated phantom were measured for thermal neutron flux, capture gamma-ray and internal conversion electron dose rates for gadolinium neutron capture therapy. The results show that (i) a significant dose enhancement can be achieved in the tumor by capture gamma-rays and internal conversion electrons but the dose is mainly due to capture gamma-rays from the Gd(n,γ) reactions, therefore, is not selective at the cellular level, (ii) the dose distribution was a function of strongly interrelated parameters such as gadolinium concentrations, tumor site and neutron beam size (collimator aperture size), and (iii) the Gd-NCT by thermal neutrons appears to be a potential for treatment of superficial tumor.

INTRODUCTION

The isotope gadolinium (157Gd) has been suggested as an alternative neutron capture therapy (NCT) agent to 123I). Possible advantages of Gd-NCT are as follows: (i) thermal neutron cross sections (245,000 barn) for 157Gd is 66 times larger than that of 123I. (ii) gadolinium neutron capture reactions produce prompt gamma-rays with relatively low energy accompanying by emission of low energy conversion electrons (Fig. 1(a) and (b)) and Auger electrons. (iii) gadolinium is used as a contrast medium for magnetic imaging (MRI) in the form of gadopentetate meglumine (Gd-DTPA) and may lead to an effective Gd-NCT compound.

In a previous communication2), we reported the radiation effect of Gd neutron capture reactions in cultured Chinese hamster cells. Comparison of the results at 10% survival level between cell cultures with and without Gd showed 3.5-fold difference in the neutron fluence. We also calculated the depth-dose distributions for thermal and epithermal neutron fluxes and capture gamma-ray dose rate using a two-dimensional neutron coupled gamma-ray transport code (DOT3.5)3). The results showed that (i) a capture gamma-ray dose rate of 10 Gy/h was obtained with a thermal neutron flux of 1.5 x 10^5 ncm^-2s^-1 in a simulated tumor containing 5,000 ppm Gd placed near the
surface of water phantom, (ii) deep-seated tumor can be treated with epithermal neutrons, and (iii) Gd-NCT appears to achieve comparable dose distributions to those of boron neutron capture therapy.

In this paper, the depth-dose distributions for thermal neutron flux, capture gamma-ray and internal conversion electron dose rates have been measured in a cylindrical phantom with a simulated tumor containing Gd in terms of Gd concentrations, neutron beam size (collimator aperture size) and tumor site.

Figure 1. Yields of capture gamma-rays (a) and internal conversion electrons (b) taken from the data of Greenwood et al. (1978)
EXPERIMENT

The phantom experiments were performed at the irradiation port in the experimental beam hole (7R) of JRR3M. Gold activation analysis shows that the thermal neutron flux in the beam at the irradiation position is $2 \times 10^7$ ncm$^{-2}$s$^{-1}$ and Gd ratio is 400. The gamma-rays decreased to 3 cGy/h dose rate to soft tissue by inserting the bismuth filters (15 cm thick) into the beam. The cylindrical phantom used was 16 cm in diameter and 17 cm in length and was filled with water except for the central region (3 cm x 3 cm x 16 cm) into which a detector holder can be inserted for measurement of the thermal neutron flux, gamma-rays and internal conversion electrons (Fig. 2a and b). The thermal neutron flux and gamma-ray dose rate were measured by an activation method of gold foils and thermoluminescence dosemeters (TLD), respectively. In order to measure the internal conversion electron dose, two sets of film (Fuji FR film) measurement were carried out. One set was made with a film covered by an aluminum foil (50 µm). The other set was made with bare films. The first set of measurements provides the information of Gd capture gamma-ray only and the second set revealed the combined effect of capture gamma-rays and internal conversion electrons. The entire phantom and a detector holder were covered with thin aluminum tape to keep darkness. Two characteristic curves, one is gamma-rays and the other electrons, to obtain the dose from the optical density in films were obtained by using a $^{60}$Co source which was made from CoCl$_2$ in HCl solution. The source emits average energies of 1.25 MeV gamma-rays and 100 keV beta-rays which correspond to the energy of capture gamma-rays and internal conversion electrons from the gadolinium neutron capture reactions, respectively.

A flexible sheet that contained $^6$LIF was used to collimate thermal neutron beam entering into the phantom. The diameter of the collimator aperture varied to 0, 5, 10 and 15 cm. The effect of Gd concentrations in the tumor were examined at various levels (0, 100, 500, 1000 and 5,000 ppm) and tumor sites were changed from the surface to deep-regions in a phantom.

Figure 2. Phantom and two detector holders used for the experiments. The holder A was used for gold foil and TLD setting. The holder B was used for film method.
RESULTS AND DISCUSSION

Figure 3(a) and (b) show the distributions of thermal neutron flux and gamma-ray dose rate along the central axis of the phantom with a simulated tumor at a depth of 2-5 cm containing 1,000 ppm Gd when changing the collimator aperture size from 0 to 15 cm. Thermal neutron flux distributions varied depending on the neutron aperture sizes. Improved penetration of thermal neutrons and increased gamma-ray dose rate were associated with a large collimator. The latter is due to the capture gamma-rays from the Cd(n, γ) reactions which occurred in the tumor region. When the collimator aperture was closed the measured value was only the core gamma-ray dose because thermal neutrons were decreased to 1/100 and did not produce the capture gamma-rays.

Figure 4(a) and (b) show the distributions of thermal neutron flux and gamma-ray dose rate along the central axis of the phantom with a simulated tumor at a depth of 2-5 cm containing different Gd concentrations. As the Gd concentrations in the tumor increased, the thermal neutron flux across the tumor decreased, and the capture gamma-ray dose increased. The capture gamma-ray dose rate at 0 ppm Gd was solely due to H(n,γ)D reactions. At 1,000 ppm Gd the dose rate across the tumor increased to 10

Figure 3. Distributions of thermal neutron flux (a) and gamma-ray dose rate (b) along the central axis of the phantom with a simulated tumor at a depth of 2-5 cm containing 1,000 ppm Gd in terms of a neutron beam size.
Figure 4. Distributions of thermal neutron flux (a) and gamma-ray dose rate (b) along the central axis of the phantom with a simulated tumor at a depth of 2-5 cm containing four different Gd concentrations.

Gy/h, 2.5 times greater than that at 0 ppm Gd. A linear relationship was not observed between the Gd concentration and the capture gamma-ray dose rate in the tumor because of thermal neutron depression at higher Gd concentrations.

Figure 5(a) and (b) show the distributions of thermal neutron flux and gamma-ray dose rate along the central axis of the phantom when changing a tumor site from a depth of 1-4 cm to 4-7 cm containing 5,000 ppm Gd. The thermal neutron flux and gamma-ray dose rate distributions varied depending on the tumor site. The gamma-ray dose rate decreased as a tumor site at a deep region from the surface. However, it is interesting that the capture gamma-ray dose rate of 25 Gy/h can be obtained at a tumor site of 1-4 cm by associating of $4 \times 10^9$ ncm$^{-2}$s$^{-1}$ thermal neutron flux.

Figure 6(a) and (b) show the results of film measurements in a simulated tumor at a depth of 1-4 cm containing 1,000 ppm Gd in comparison with the gamma-ray dose rate distribution. A significant difference was observed in the optical density between the bare film and the aluminum covered film. However, the electron dose rate converted from the optical density by using the characteristic curves was found to be 20 times smaller than that of capture gamma-ray dose rate. It is estimated that only electrons around the surface of the film correspond to dose deposited because of its short range (100 μm in water) of conversion electrons.
Figure 5. Distributions of thermal neutron flux (a) and gamma-ray dose rate (b) along the central axis of the phantom when changing a tumor site from a depth of 1-4 cm to 4-7 cm containing 5,000 ppm Gd.

Figure 6. Optical density (a) and dose rate (b) distributions obtained by film measurements in a simulated tumor at a depth of 1-4 cm containing 1,000 ppm Gd.
CONCLUSIONS

A significant dose enhancement can be achieved in the tumor by capture gamma-rays and internal conversion electrons but the dose is mainly due to the capture gamma-rays from the \textit{Cd(n,\gamma)} reactions, therefore, is not selective at the cellular level. The dose distribution was a function of strongly interrelated parameters such as gadolinium concentrations, tumor site and neutron beam size (collimator aperture size). The Gd-NCT by thermal neutrons appears to be potential for treatment of superficial tumor.

ACKNOWLEDGEMENT

This research was supported by Grant-in-Aid from the Ministry of Education, Science and Culture.

REFERENCES

PROMPT GAMMA-RAY SPECTROMETRY FOR MEASUREMENT OF
B-10 CONCENTRATION IN BRAIN TISSUE AND BLOOD
- CLINICAL USE AND EXPERIMENTAL STUDY-

1) Yoshinobu NAKAGAWA, Katsuji KITAMURA, 2) Toru KOBAYASHI
3) Keizo MATSUMOTO and 4) Hiroshi HATANAKA

1) Department of Neurosurgery, National Kagawa Children's
   Hospital, Zentsujicho 2603, Zentsuji-shi, Kagawa 765, Japan
2) Research Reactor Institute, Kyoto University
   Kumatori-cho, Sennan-gun, Osaka 590-04, Japan
3) Department of Neurosurgery of Tokushima University
   Kuramoto-cho, Tokushim-ashi, Tokushima 776, Japan
4) Department of Neurosurgery of Teikyo University
   Kaga 2-chome, Itabashi-ku, Tokyo173, Japan

ABSTRACT

Boron-10 (B-10) concentration in the brain tissue and blood was measured
continuously for 24 hours after injection of the B-10 compound in live
rabbits using prompt gamma-ray spectrometry. Following injection of B-10
compound (Na2B12H11SH, 50mg/kg) dissolved in physiological saline, B-10
concentration was continuously measured in the brain tissue. Intermittently
the concentration of B-10 in blood and cerebro-spinal fluid (CSF) was also
measured. In 10 minutes after the injection of B-10 compound, the level of
B-10 concentration reached the peak of 400-500 ppm in blood and 20-30 ppm
in the normal brain tissue. In 60 minutes the level of B-10 concentration
rapidly decreased and then a gradual decline was observed. The value was 15-
30 ppm at 3 hours after injection, 5-10 ppm at 6 hours and 2-5 ppm at 24
hours in the blood. The concentration in the brain tissue was 3-8 ppm at 3
hours, 2-5 ppm at 6 hours and below 1.5 ppm at 24 hours. B-10 concentration
in cerebro-spinal fluid was below 1 ppm.
B-10 concentration was also measured in the brain tumor and blood in the human cases at boron neutron capture therapy (BNCT). These data studied by prompt gamma-ray spectrometry are very important and useful to decide the irradiation time.

INTRODUCTION

For boron neutron capture therapy, irradiation time depends on greatly on neutron flux and B-10 concentration in blood, brain and brain tumors. Neutron flux can be measured by simultaneous monitoring (acoustic pulse generation: Hayakawa 1986) or gold wires and foils placed where they are necessary for neutron monitoring. Therefore, to estimate clinical effect and to prevent damage of the normal brain tissue, it is indispensable to measure the B-10 concentrations in tumor and blood just before irradiation. In the former cases, B-10 concentration has been measured by chemical analysis. However, it was not easy to obtain the results during the irradiation. On the other hand, prompt gamma-ray spectrometry can measure B-10 concentrations within 10 minutes for 1g sample. The current this method has a possibility to apply to direct measurement of B-10 concentration of tumor in a patients without any pretreatment and without large damage. In this study, we tried to measure the B-10 concentration of live animals and then we used it in the clinical cases.

EXPERIMENT

Adult New Zealand rabbits (n=6) of either sex weighing approximately 3 to 3.5kg were used in this study. Under general anesthesia by intravenous injection of pentobarbital (30mg/kg iv), a small burr hole (Ca.7mm in diameter) was perforated in the right parietal region of the skull using a dental drill. The brain surface covered by dura mater was coagulated and the animals were fixed to the measuring system. This technique was developed by one of our authors (T.K 1983) and can measure boron-10 concentrations of ppm order. The detection range of the system is 0.1-0.5ppm boron concentration. The neutron guide tube of KUR has a guide part of 9.9m and a neutron beam size of 10 mm (width) X 74 mm (height). The fluence rate of thermal neutrons is $2 \times 10^4$ n/cm$^2$/sec with a gamma ray contamination of about 1mR/h at an opening power of 5MW. The details of the prompt gamma-ray spectrometry were previously described (Kobayashi & Kanda 1981). A thermal neutron beam collimated by 6LiF tile with 5mm in diameter was delivered to the brain surface through the burr hole. Following intravenous injection of the boron compound (Na2B12H11SH, 50mg/kg) diluted in physiological saline, gamma emission from the target point on the surface of the brain was measured continuously. The
measuring time was 600 seconds. Blood samples (1ml) were intermittently drawn and was also studied. In 3 animals the atlant-occipital membrane was exposed following the midline skin incision and cerebro-spinal fluid (CSF) was also obtained. These materials were collected in a pure teflon tube for boron-10 analysis. After all procedures, the animals were sacrificed at different time intervals (5, 8, 9 and 24 hours after injection of the boron compound) by venous injection of KCl(1mole : 10ml). The brain was immediately removed and the brain tissue was divided into four parts: cerebral cortex, cerebellar cortex, brain stem and basal ganglia. These materials were collected in pure teflon tubes and the boron-10 concentration of each area was measured by the same method.

CLINICAL STUDY

Blood and tumor samples were obtained from 15 patients (11 men and 4 women, raging age from 1 years to 76 years) who underwent boron neutron capture therapy at KUR between February 1990 and November 1992. All samples were collected in pure teflon tubes and the B-10 concentration was measured by prompt gamma ray spectrometry during BNCT. The measuring time was 300 seconds.

RESULTS

The standard samples with various B-10 concentrations 1, 10 and 30 ppm were made by diluting the JIS standard solution. \(^{10}\)B/H (ratio of gamma radiation from boron-10 to gamma radiation from hydrogen in tissue) of the standard samples were used to calculate the boron-10 concentration of all samples. However, the concentration of boron and hydrogen might not be homogeneous in biological samples, so that the boron-10 concentration of brain tissue of live animals was demonstrated in terms of \(^{10}\)B/H (Fig. 1). In 10 minutes after the injection of the compound, the boron-10 concentration reached its peak. In 60 minutes the level of the boron-10 concentration rapidly decreased and then a gradual decline was observed. At 3 hours, the value of \(^{10}\)B/H was 0.2-0.4 and at 5 hours the ratio was 0.1-0.2. After 12 hours the mean ratio of \(^{10}\)B/H was below 0.1. The boron-10 concentration of blood showed similar changes as in brain tissue (Fig. 2). In 10 minutes after the injection of the boron-10 compound, the level of boron-10 concentration reached the peak of 400-500 ppm. In 60 minutes the level of boron-10 concentration in blood rapidly decreased and afterwards a gradual decline was observed. The value was 15-30ppm at 3 hours after injection, 5-10ppm at 6 hours and 3-8ppm at 18 hours in the blood (Fig 1). On the other hand, boron-10 concentration in brain tissue of the sacrificed animals showed lower value. In the cerebral cortex it was below 1 ppm 5 hours after injection of the
boron-10 compound. Only in the brain stem, boron content of 3 ppm was noted at 5 hours (Fig. 3). Boron-10 concentration in the cerebro-spinal fluid was below 1 ppm in all animals (Table1).

Clinically, the attenuation of boron concentration in patient's blood was similar to that in the experimental model (Fig 3). In all cases irradiation was performed under the B-10 concentration between 7 ppm-15 ppm. Tumor to blood ratio of the B-10 concentration was 1.5-2.7 (Fig. 4, 5)

DISCUSSION

The radiation doses in the tumor and in the normal brain of a patient treated by BNCT are determined by neutron fluence and concentration of B-10 in the tumor and in the blood. Neutron intensity in the brain is influenced by many factors, such as the distance between the patient's head and the irradiation port, the size of the irradiation field, and the depth of the tumor. The time course of the change of B-10 concentration in blood showed a similar pattern in each patient. However, it is also influenced by such factors as patient's physiological condition, age, dehydration, renal function and injection speed of the B-10 compound. Therefore in situ measurement of B-10 concentration of brain tumor and normal brain tissue around the tumor during the irradiation of patients is essential for a successful BNCT. In this study we investigated the gamma emission ratio $^{10}$B/H of the brain tissue of live rabbits using prompt gamma ray spectrometry and compared the value to that of blood. In in vitro study, the concentration of boron and hydrogen can be assumed to be homogeneous in the tissue, so that prompt gamma rays emitted from hydrogen can be used for the normalization. It is yet difficult to estimate the accurate standard data for in vivo study. In this study, B-10 concentration of the brain tissue was demonstrated using the ratio of B-10 to H (hydrogen) and the absolute value was not obtained. In this measuring system B-10 concentration was determined by comparison with known sample data: ratio of B-10 to H. If we compare the ratio of in situ $^{10}$B/H with that of the in vitro study, 10 ppm corresponded to 0.54+0.03 in $^{10}$B/H. If so, the B-10 concentration in the brain tissue of a live animal was 3-5 ppm. However, the B-10 concentration of the sacrificed brain tissue at the same time interval was below 1 ppm. This discrepancy may be caused by the differences of blood volume between the live brain and the sacrificed brain and the surrounding tissues such as dura mater and bone which contain different concentration of boron and hydrogen. There are still a few problems to make control models. However, gamma ray spectrometry will be a very useful method, not only for experimental use but also for clinical purpose.

This work has been carried out in part under the Visiting Researcher's Program of the Research Reactor Institute, Kyoto University.
REFERENCES
Kobayashi T and Kanda K. : Microanalysis system of ppm-order 10B concentration in tissue for neutron capture therapy by prompt gamma-ray spectrometry, Nuclear Instruments and Methods 204:525-531, 1983


Fig. 1 Boron-10 concentration in brain tissue

Fig. 2 Boron-10 concentration in blood (n=6)
Fig. 3  Boron-10 concentration in the brain (ppm, n=6)

Table 1. Boron-10 concentration in cerebro-spinal

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>(B) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.94</td>
</tr>
<tr>
<td>6</td>
<td>0.51</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>0.05</td>
</tr>
<tr>
<td>24</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Boron-10 compound was given by intravenous injection (50mg/kg)
CSF was collected from cisterna magna
Boron concentration was measured by prompt gamma ray spectrometry.
D2O was measured by infrared spectroscopic analysis.

**Fig. 4** The time course of the changes of B-10 concentrations in the blood (Case 7)

---

measured by prompt gamma ray spectrometry

20.2 ppm in the tumor just before irradiation

**Fig. 5** Boron -10 concentrations in the blood (Case 9)
BORON NEUTRON CAPTURE THERAPY FOR CHILDREN
WITH MALIGNANT BRAIN TUMOR

1) Yoshinobu NAKAGAWA, Hisao KOMATSU, Teruyoshi KAGEJI
2) Fumio TSUJI, 3) Keizo MATSUMOTO, Katsuji KITAMURA and
4) Hiroshi HATANAKA , Takashi MINOBE

1) Department of Neurosurgery and Anesthesiology, National Kagawa
   Children’s Hospital, Kagawa 765, Japan
2) Department of Anesthesiology, National Okayama Hospital
3) Department of Neurosurgery of Tokushima University
4) Department of Neurosurgery and Anesthesiology of Teikyo University

ABSTRACT

Among the 131 cases with brain tumors treated by boron-neutron capture therapy (BNCT), seventeen were children. Eight supratentorial tumors included five astrocytomas (grade 2-4), two primitive neuroectodermal tumors (PNET) and one rhabdomyosarcoma. Seven pontine tumors included one astrocytoma, one PNET and 5 unverified gliomas. Two cerebellar tumors (PNET and astrocytoma) were also treated. All pontine tumors showed remarkable decrease in size after BNCT. However, most of them showed regrowth of the tumors because the neutrons were insufficient due to the depth. Four cases with cerebral tumor died of remote cell dissemination, although they all responded to BNCT. One of them survived 7 years after repeated BNCTs. An 11 years old girl with a large astrocytoma in the right frontal lobe has lived more than 11 years and is now a draftswoman at a civil engineering company after graduating from a technical college. An 8 years old girl with an astrocytoma in the left occipital lobe has no recurrence of the tumor for 2 years and attends on elementary school without any mental and physical problems. Two children (one year old girl and four years old boy) with cerebellar tumors have shown showed an excellent growth after BNCT and had no neurological deficits. Mental and physical development in patients treated by BNCT is usually better than that in patients treated by conventional radiotherapy.
INTRODUCTION

Boron neutron capture therapy (BNCT) is an ideal radiotherapy for brain tumors in children, because mental and physical development in children treated by BNCT is usually better than in patients treated by conventional radiotherapy. However, there are more cases with deep-seated brain tumors, such as brain stem gliomas and periventricular tumors in children than in adult. It is also widely believed that thermal neutrons can not ideally treat a patient with deep-seated brain tumors because of the attenuation of neutron flux in the brain tissue. In such a case, deuteration of brain water content and/or multiportal radiation should significantly improve neutron penetration in the tissue and can be used to treat deep-seated brain tumors.

MATERIAL AND METHOD

Patients: until December, 1992, we have treated eighteen children with malignant brain tumor ranging in age from one to 16 years of age. Eight supratentorial tumors included five astrocytomas (grade 2-4), two primitive neuroectodermal tumors (PNET) and one rhabdomyosarcoma. Eight pontine tumors included two astrocytomas, one PNET and 5 unverified gliomas. Two cerebellar tumors (PNET and astrocytoma) were also treated (Table 1).

Procedure: The boron-10 compound used in this study since 1968 is mercaptopendecahydrodecaborate (Na2B12H11SH) made from 95-97% enriched boron-10 (abbreviated as BSH or borocatate). Isotonic aqueous solution of the boron compound (50-60mg/kg) is added to an equal volume of physiological saline and is infused into the carotid or vertebral artery with a pressurized motor pump or by a simple intravenous drip. The infusion of boron-10 is done 8-14 hours before neutron irradiation. No complication was encountered except for a mild flushing of the face when the infusion speed is too fast. Infusion usually takes 30-60 minutes. The patients whose tumors had been debulked by craniotomy a week or two earlier, are taken to the reactor. Samples of blood and urine are collected for boron chemical analysis or for prompt gamma-ray spectrometry.

In the reactor a patient undergoes general anesthesia and the skin flap is re-opened. The bone flap is usually removed during the procedure to obtain tumor tissue specimens for pathology and boron analysis. In case of deep-seated tumor or brain stem tumor in which heavy water replacement is carried out, physical saline solution made of D2O is infused into the ventricles while the cerebrospinal fluid is drained. Gold wires and foils and simultaneous monitoring devices are placed where they are necessary for neutron monitoring. The whole head is covered with a sterilized plastic 6LiF helmet except for the area to be radiated. The entire head
is covered with a sterile plastic film to void contamination. The operating table together with the patients is rolled into the radiation room to place that head against the beam. All the vital sign monitoring devices are connected to the body. The door is closed, and the neutron beam is delivered to the tumorous area. The irradiation time is calculated so that the deepest part of the tumor will be given at least 10 Gy (or 1000 rad) and that the superficial layer of the normal cerebral surface will be exposed to less than 20 Gy (or 2000 rad). After the whole procedure, the head is closed as in routine craniotomy.

RESULT

Four children with supratentorial tumors died of remote cell dissemination, although they all responded to BNCT. One of them survived 7 years after repeated BNCT. An 11 years old girl with a large astrocytoma in the right frontal lobe has lived more than 11 years and is now a draftswoman at a civil engineering company after graduating from a technical college. An 8 years old girl with astrocytoma in the left occipital lobe has no recurrence of the tumor for 2 years and attend on elementary school without mental and physical handicaps. All pontine tumors showed remarkable decrease in size after BNCT. However, most of them showed regrowth of the tumors because the neutrons were insufficient due to the depth. Two children (one year old girl and four years old boy) with cerebellar tumors showed excellent improvement after BNCT and have no neurological deficits nor mental retardation. The recent development of diagnostic means such as CT or MRI permits precise localization of the tumor and thereby helps to determine the radiation field and neutron fluence.

Case Reports

Case 9: An 11 year-old boy. Ventricular dissemination of primitive neuroectodermal tumor (PNET). The patient had headache and vomiting in June, 1984 and on August 23, 1984 underwent craniotomy to remove a tumor in the left occipital area. Histologically it was PNET and irradiation was performed. Whole spine was also radiated. Subsequently this patient did well for 3 years, and then he suddenly started deteriorating in July, 1987. This time the original tumor site was empty, but multiple nodules were found in the bilateral ventricle and the third ventricle. He was referred to one of the authors (H.H.) for BNCT. The ventricles were were lined with nodular masses (Fig 1-a). On August 21, at Musashi Institute of Technology Reactor, the patients underwent BNCT.

A total of 2500ml of heavy water in the form of isotonic glucose and saline solution was given intravenously during the general anesthesia for BNCT. This yielded a 7% replacement rate on
the average. The beam was introduced from the left parietal region, then the direction was changed and the beam was introduced from the occipital region. As the result, the gold wire measurement was 8.0 X 108 n at the occipital surface, 2.8 x 10E8 n at 6 cm from the cranial surface (= foramen Monro), and 2.6 x 10E8 n at 8 cm below the cranial surface (= IIId ventricle). Estimated dose to the tumor was 1400-1300 cGy or 4100-3800 RBE dose; to the brain 1100-300 cGy or 1100-300RBE dose. The patient recovered promptly after BNCT, and MRI made on September 25 within 35 days after BNCT, showed a prompt regression of the tumor. A total of 2000 cGy was radiated over the posterior fossa and the spine with a lineal accelerator. A follow up scan made on October 7 showed no more tumor nodules (Fig. 1-b). He enjoyed a happy family life for a while, but then he started deteriorating due to the radiation damage which was the result of overlapped radiotherapies. Radiation was evidenced in the cerebral white matter in the later CT. He died 1.5 years after BNCT.

Case 11: A 2 years old male. PNET in the brain stem. Ataxic gait and left facial paresis were noted by pt's mother in April 1989. A large mass was demonstrated in the brain stem by CT and MRI(Fig. 2-a, b). On June 2, the patient underwent BNCT at Musashi Institute of Technology. Before the neutron irradiation, ventricular drainage was carried out through the right occipital horn of the lateral ventricle. Then heavy water physiological saline solution was circulated in the subarachnoid space from the lateral ventricle to cisterna magna. Neutron irradiation was performed from one direction and followed by the conventional radiotherapy (3000 cGy). The patient recovered completely after treatment and MRI demonstrated remarkable decreasing in size of the tumor (Fig. 3-a,b). He had no neurological deficits until a six months after BNCT. He became unable to walk and had vomiting due to hydrocephalus. Recurrence of the tumor was suspected and chemotherapy (5-FU) was given for 14 days by a pediatrician in another university. He suddenly deteriorated and died. Autopsy revealed an Intratumoral hemorrhage. He died 264 days after BNCT.

Case 16: A one year old female. PNET in the cerebellum. In June 1992 the child was seen by a pediatrician because of gait disturbance (cerebellar ataxia). A large cystic mass was demonstrated in the posterior fossa by CT and MRI. The wall of the cystic tumor was irregularly enhanced (Fig. 4-a). Following the suboccipital craniotomy, the tumor was partially removed. Histological diagnosis was PNET. On July 13 the patient underwent BNCT at Kyoto University Reactor. Following the suboccipital craniotomy, a gold wire was placed in the tumor and neutron flux was measured. As the result, the neutron flux was 2.9 X 10E8 n at the deepest area of the tumor and 6.6 x 10E8 n at 6 cm from the cranial surface (cerebellum). Boron
concentration in the tumor was measured by prompt gamma-ray spectrometry and the value was 28.6ppm. According to the data, the irradiation time of 192 minutes was decided. The patient recovered completely after BNCT and the tumor remarkably decreased in size (Fig 4-b). She has no neurological deficit and shows a good mental and physical development.

REFERENCES

1) Kobayashi M., Decrease in Deuterium Content of Heavy Water in Contact with Air. Annual reports of the Research Reactor Institute, Kyoto University, Vol 23, p188-193

Figure 1-a. MRI (before BNCT)
High intensity mass was demonstrated around the ventricular wall.

Figure 1-b. MRI (after BNCT)
Dilated ventricular system with smooth ventricular wall. Tumor mass completely disappeared.
Figure 2-a. MRI (before BNCT): Enhanced mass lesion with cyst was demonstrated in the brain stem (T-1 Gd+)

Figure 2-b. MRI (before BNCT): Enlarged brain stem with cystic lesion was demonstrated

Figure 3-a. MRI (after BNCT): Cystic lesion completely disappeared
Figure 3-b. MRI (2 months after BNCT): The tumor decreased in seize. No enhanced lesion was demonstrated. (T-1, Gd+)

Figure 4-a. (before BNCT) Markedly enhanced tumor was revealed. Note the depressed IVth ventricle and brain stem.

Figure 4-b. (2 months after BNCT) The tumor remarkably decreased in size IVth ventricle showing normal size and form.
<table>
<thead>
<tr>
<th>case no.</th>
<th>age</th>
<th>site</th>
<th>histology</th>
<th>survival(days)</th>
<th>cause of death</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>pons</td>
<td>not verified</td>
<td>339</td>
<td>regrowth</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>cerebral</td>
<td>rhabdomyosarcoma</td>
<td>2460</td>
<td>dissemination</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>pons</td>
<td>astrocytoma II</td>
<td>1833</td>
<td>negligence in shunt revision, (no tumor; isolated 4th ventricle)</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>pons</td>
<td>not verified</td>
<td>209</td>
<td>regrowth</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>cerebral</td>
<td>astrocytoma II</td>
<td>1277</td>
<td>autoimmune disease =leucoencephalopathy (no tumor)</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>pons</td>
<td>not verified</td>
<td>159</td>
<td>regrowth</td>
</tr>
<tr>
<td>7</td>
<td>11</td>
<td>cerebral</td>
<td>astrocytoma II~III</td>
<td>&gt;11 years</td>
<td>alive and well</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>pons</td>
<td>not verified</td>
<td>95</td>
<td>regrowth + radiation myelitis</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>ventricle</td>
<td>PNET</td>
<td>1607</td>
<td>radiation myelitis (due to earlier radiotherapy)</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>cerebral</td>
<td>glioblastoma</td>
<td>355</td>
<td>dissemination</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>pons</td>
<td>PNET</td>
<td>264</td>
<td>hemorrhage in tumor</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>pons</td>
<td>not verified</td>
<td>187</td>
<td>dissemination</td>
</tr>
<tr>
<td>13</td>
<td>6</td>
<td>ventricle</td>
<td>astrocytoma III</td>
<td>679</td>
<td>dissemination</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>thalamus</td>
<td>PNET</td>
<td>303</td>
<td>dissemination + malpractice</td>
</tr>
<tr>
<td>15</td>
<td>8</td>
<td>cerebral</td>
<td>astrocytoma III</td>
<td>&gt;2 years</td>
<td>alive and well</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>cerebellar</td>
<td>astrocytoma III</td>
<td>&gt;7 months</td>
<td>alive and well</td>
</tr>
<tr>
<td>17</td>
<td>4</td>
<td>cerebellar</td>
<td>PNET</td>
<td>&gt;5 months</td>
<td>alive and well</td>
</tr>
</tbody>
</table>

10 years survival = 1/8 = 12.5%  5 year survival = 3/9 =33.3%
STRUCTURE ANALYSIS OF $K_3H(SO_4)_2$ BY NEUTRON POWDER DIFFRACTION

*Satoshi MURAKAMI, *Yoshihiro KUROIWA, *Yukio NODA, *Yusuke NAKAI, *Takashi KAMIYAMA and *Hajime ASANO

*Faculty of Science, Chiba University, Yayoi, Inage, Chiba 263, Japan

*Institute of Materials Science, University of Tsukuba, Tennoudai, Tsukuba 305, Japan

ABSTRACT

Neutron powder diffraction experiments of $K_3H(SO_4)_2$ were carried out at KEKNS-HRP station in order to obtain the positional parameters of hydrogen nuclei. The data was taken at six different temperatures from room temperature to 20K. Even though $K_3H(SO_4)_2$ contained a hydrogen atom, the structural analysis was successfully performed by using a program Rietan. Concerning the hydrogen position, four different models give almost the same R-factor so that the state of the hydrogen nucleus is not uniquely determined. The result based on the assumption that a hydrogen nucleus occupies two sites shows that the distance of split hydrogen nuclei is shorter than the distance of hydrogen electron clouds. This result suggests that a large polarizability exists in a hydrogen atom.

INTRODUCTION

The isotope effect of $K_3H(SO_4)_2$ was extensively studied so far, since this compound has a very simple structure of a hydrogen bonding (Fig.1) and shows a large isotope effect. Deuterium compound has a phase transition at $Tc(D)=85K$, while a hydrogen compound has no phase transition point ($Tc(H)<0K$). $1-9$ The hydrogen bond is isolated in a crystal forming a SO$_4$ dimer, and thus this system is called a zero dimensional hydrogen bond system. X-ray structural analyses revealed that the hydrogen atoms took two peak behavior on a differential Fourier synthesis map not only in the D-compound but also in the H-compound as depicted in Fig.2. The precise temperature dependence of the structure of $K_3H(SO_4)_2$ is also reported. $10$ The electron cloud of the hydrogen atom gradually change from two peaks behavior to one peak behavior on decreasing temperature, and the hydrogen bond length accidentally crossed a critical bond length $r_c(H)=2.478A$ at about 100K.

An X-ray structural analysis can determine a position of electron density and not a position of nucleus. Dose a hydrogen nucleus show also two peak behavior? According to literatures, positions of hydrogen atoms determined by X-ray experiments are systematically different from positions of hydrogen atoms determined by neutron experiments. A hydrogen bond length $R_{HH}$ determined by neutron has a tendency to be shorter than $R_{HH}$ determined by X-ray. In some case, a hydrogen electron cloud shows two peak behavior but its nucleus shows one peak behavior. The purpose of the present experiment is to determine the position of the hydrogen nucleus of $K_3H(SO_4)_2$ in order to study the origin of the isotope effect in hydrogen bond materials.
EXPERIMENTS AND ANALYSIS

Neutron powder diffraction of \( \text{K}_2\text{H} (\text{SO}_4)_2 \) were carried out at the XENS-HRP station. In general, neutron coherent scattering experiment of materials containing a hydrogen atom is difficult because strong incoherent neutron scattering from hydrogen atoms becomes a background. In addition, powder diffraction has less signal to noise ratio compared with a single crystal experiment. Usually, experiments are carried out after permutation from H-atom to D-atom. The purpose of the present study is to investigate a position of H-atom nucleus, so that, permutation to D-atom is out of the scope. The hydrogen compound \( \text{K}_2\text{H}(\text{SO}_4)_2 \) was used as a sample. The neutron powder diffraction data taken at the HRP station at room temperature was very good, more than expected, and the obtained intensity data were successfully analyzed by a program RIETAN. As a next step, we carried out experiments at six different temperatures from room temperature to 20K.

Fig. 3 shows an observed and calculated profile given by the program RIETAN. In this figure, cross marks give obtained data subtracted back-

Fig. 4 A differential Fourier map shows the density of hydrogen nucleus. The ratio of the height to the side of the figure is not properly drawn. A dotted line shows negative value corresponding to a scattering amplitude of hydrogen nuclei for neutron.
ground, and a solid line shows calculated value by RIETAN. Difference between observed and calculated values are shown at Δy. The fitting seems satisfactory. Neutron diffraction has a characteristic that scattering amplitude of oxygen atom is relatively strong and scattering amplitude of H-atom has a negative value.

As the first step of the analysis, we constructed differential Fourier synthesis map by using the difference between the observed structure factors and the calculated ones without the hydrogen atom in order to check that hydrogen atom exists between hydrogen bonding. Fig.4 is the differential Fourier map showing the density of hydrogen nuclei. In the figure, a dotted line shows a negative value corresponding to a negative scattering amplitude of an H-atom. Certainly, a hydrogen nucleus exists in the center of two oxygens forming a hydrogen bond. Our interest is whether the hydrogen nucleus takes two site behavior or sits at the center of the bond. Unfortunately, we cannot discuss this point from Fig.4, because the number of independent F(HKL) in Rietveld method is very few compared with an ordinary structural analysis by a single crystal. Therefore, we performed the structural analysis based on the following several structural models concerning the hydrogen state. (1) A hydrogen nucleus exists in a center of symmetry with harmonic vibration. (2) A hydrogen nucleus exists in a center of symmetry with anharmonic vibration. (3) Split hydrogen nuclei exist in two positions with harmonic vibration. (4) Split hydrogen nuclei exist in three positions given by the above models (1) and (3). The obtained R-factors based on these four different models are essentially indistinguishable except model (1). The R-factor of model (1) is apparently worse than those in other models. The number of fitting parameter are 69, 74, 72 and 73 respectively so
that model (3) is somehow plausible among them. Further, obtained positional parameters for oxygen atoms in model (3) seems to be more consistent with the results determined by the X-ray structural analysis, as shown in Fig.5.

In order to discuss the position of a hydrogen nucleus, we use the results given by model (3). Anharmonic vibrations are only applied to oxygen atoms. In other words, we assume split hydrogen nuclei to investigate the distance of two sites. Note that, in this model, the length between hydrogen nuclei RH is usually non zero value. Figs.5 and 6 show R00 and RH as a function of temperature. In Fig.7, R00 vs. RH are summarized. The distance of split hydrogen nuclei is 0.42A at room temperature and decreases down to 0.375A at 150K. These numbers must be compared with the distance of hydrogen electron clouds as 0.55A at room temperature and 0.51A at 150k. Thus, experimental results indicate that the electron clouds are pulled to oxygen atoms. This means that a hydrogen atom has a large polarizability in the hydrogen bond region.

CONCLUSION AND DISCUSSION

In the present experiment, we could successfully analyze the structure of the hydrogen compound K3H(SO4)2 by the neutron powder diffraction. Concerning the hydrogen nuclei, we cannot determine the state of position uniquely. The analysis based on the assumption that a hydrogen nucleus has two site behavior gives the result that the distance of hydrogen nuclei is shorter than the distance of hydrogen electron clouds. Such difference is generally observed in other systems, and this means that a large polarizability exists in a hydrogen atom. We think that the origin of the isotope effect is related to such a polarizability of hydrogen atoms as well as its electron state. And the difference of the electron between H and D must be understood by the motion of H and D nuclei.

REFERENCES

STUDY OF NEUTRON MEDICAL IRRADIATION FACILITY WITH SUPERMIRROR NEUTRON GUIDE TUBE IN JRR-3M

Kazuhiko SOYAMA, Masatoshi SUZUKI, Yuji KAWABATA* and Hiroki ICHIKAWA

Department of Research Reactor
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki, 319-11 Japan

*Research Reactor Institute
Kyoto university
Kumatora-cho, Sennan-gun, Osaka, 590-04 Japan

ABSTRACT

A medical irradiation facility using a supermirror guide tube has been designed for boron neutron capture therapy (BNCT) treatment at the JRR-3M. Intense thermal neutrons are obtained with lower fast neutrons and gamma rays contamination at the end of neutron guide tube. It would be a most suitable neutron field for BNCT treatment.

INTRODUCTION

Boron Neutron Capture Therapy (BNCT) is a kind of cancer therapy, which is based on the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. The stable isotope $^{10}\text{B}$, which has a large capture cross-section for thermal neutron (about 25meV), capture neutron and the isotope become unstable and generate $^7\text{Li}$ and alpha particle ($^4\text{He}$). It release their energy within a cell (about 10microns). Fortunately, capture cross-section of the other atoms in the body, is low enough in comparison to $^{10}\text{B}$. So if boron compounds are concentrated sufficiently only in the cancer cells and thermal neutron fluence is obtained in the target area, BNCT would be the ideal therapy which kills cancer cells without damaging normal cells.

BNCT was first suggested in 1936 by Gordon L. Locher in Swarthmore college.¹ Nuclear reactor has been used as a neutron source for BNCT, which is the most suitable source for obtaining an intense thermal neutron beam. The first clinical irradiations on brain cancer, were done in 1953-1961 at the Brookhaven Graphite Reactor (BGR) and the Brookhaven Medical Research Reactor (BMRR) and the MIT reactor (MITR) using $\text{Na}_2\text{B}_10\text{O}_{16}$, $\text{C}_7\text{H}_7\text{B}_9\text{O}_4$ and $\text{Na}_2\text{B}_10\text{H}_{10}$.² But the efforts shifted from clinical trials to basic studies directed to finding alternative compounds and to improvement of the neutron beam. In Japan, clinical trials were started at the Hitachi Training Reactor (HTR) from 1968 to 1975. After that, the Musashi Institute of Technology Research Reactor (MITRR)³ was used from 1977, the Kyoto University Research Reactor (KUR)⁴ from 1974 and Japan Research Reactor No.2 (JRR-2)⁵ from 1990 have been used for clinical irradiations. Table 1 shows characteristics of the neutron irradiation facilities. In Japan, Hatanaka et al. have treated more than 100 patients with various type of brain cancer using $\text{Na}_2\text{B}_12\text{H}_1\text{SH}$ (BSH).⁶ In the treatment of skin cancer, Mishima et al. have treated ten patients who had skin level melanoma using $^{10}\text{B}$-phenylalalmine as a compound.⁷ Recently, neutron facilities have been designed and constructed at some research centers encouraged by their works.⁸⁹ In this paper, we describe a design of medical irradiation facility for BNCT. It consists of neutron guide system using supermirrors, which can provide "pure" thermal neutron beam to irradiation field.
Table 1 Characteristics of the medical irradiation facilities in Japan

<table>
<thead>
<tr>
<th>Name</th>
<th>Reactor type</th>
<th>Power (kW)</th>
<th>Thermal neutron flux (n/cm²/s)</th>
<th>Gamma dose rate (Sv/h)</th>
<th>γ/ν ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTR¹</td>
<td>Light water moderated swimming pool type</td>
<td>100</td>
<td>$0.1 \times 10^9$</td>
<td>0.3</td>
<td>10.4</td>
</tr>
<tr>
<td>JRR-3²</td>
<td>Heavy water moderated tank type</td>
<td>10000</td>
<td>$0.4 \times 10^9$</td>
<td>1.6</td>
<td>13.9</td>
</tr>
<tr>
<td>KUR</td>
<td>Light water moderated swimming pool type</td>
<td>5000</td>
<td>$4.0 \times 10^9$</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>MITRR</td>
<td>Light water moderated pool type</td>
<td>100</td>
<td>$1.3 \times 10^9$</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>JRR-2</td>
<td>Heavy water moderated tank type</td>
<td>10000</td>
<td>$1.0 \times 10^9$</td>
<td>0.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

¹) The HTR was shut down in 1975.
²) The JRR-3 was shut down in 1983.

BNCT REQUIREMENT ON IRRADIATION FIELD

BNCT requires some irradiation conditions on thermal neutron flux, neutron beam size and gamma dose rate. To destroy cancer cells by BNCT, a billion boron atoms per cell is needed in order to obtain sufficient dose in each cancer cell, and thermal neutron fluence from $10^{12}$ to $10^{13}$ per cm² is required for successful treatment. For the purpose of reducing patient's load, irradiation time should be less than 5 hours. So, thermal neutron flux is needed more than $1 \times 10^9$ n/cm²/s.

Thermal neutron fluence changes rapidly near the body surface. Kobayashi¹⁰ reported that the distribution of it depends on neutron beam size in the body. It decrease rapidly when neutron beam size is less than 5cm in diameter. Thermal neutron fluence depends on a divergence of incident neutron beam also. Thermal neutron fluence caused by a forward beam is as twice as that caused by isotropic beam at a depth of 5cm.

Fast neutrons and primary gamma rays from a reactor core and secondary gamma rays from the materials in the thermal shielding can not be neglected from the standpoint of patient's dose. It must be reduced as low as possible. Dose of these backgrounds is limited less than 1 Sv/h, and it is limited less than 10% of total dose in the actual clinical treatments, and the ideal contamination ratio of fast neutrons and gamma rays should be less than 1% which is 0.1 Sv/h.¹⁰

THERMAL NEUTRON GUIDE TUBES AT THE JRR-3M

Neutron guide tube can transport low energy neutrons from a reactor core to the neutron facilities at distant place, and can reduce the background of fast neutrons and gamma rays. So "pure" thermal neutrons are obtained at the end of neutron guide tubes, so it would be a most suitable neutron field for BNCT.

The upgraded JRR-3 (Japan Research Reactor No.3) is a pool type, light water-moderated and cooled reactor (20MW) with heavy water reflector. The JRR-3M is normally operated 9 cycles a year, each cycle consists of 26 days operation. Maximum thermal neutron flux in the heavy water reflector is $2.5 \times 10^{14}$ n/cm²/sec.¹¹ Neutron guide tubes and a cold neutron source have been installed.¹² General layout of the neutron guide tubes and neutron facilities at the JRR-3M are shown in Fig.1. The main parameters of the guide tubes are shown in Table 2. A beam hall, which is 30m wide and 50m long, gives a spacious experimental area. Two thermal neutron guide tubes (T1 and T2) are about 60m long with 2A characteristic wavelength (20meV). Three cold neutron guide tubes (C1, C2 and C3) are about 31-51m long. The characteristic wavelengths of C1 and C2 are 4Å (5meV) and that of C3 is 6Å (2meV). They are curved in the guide tunnel and shielding room and straight in the beam hall. The neutron mirrors are made of nickel sputtered borosilicated glasses. These guide
tubes consist of short straight units which are 85cm long. The length of these units is short enough to make good polygonal approximation and it is also long enough to lessen for a number of conjunctions.

Beam cross-section of the thermal guide tubes is 20mm x 200mm. Thermal neutron flux at the beam shutter of the T1 guide tube in the guide tunnel which was measured by gold foil activation method, was $8 \times 10^9$ n/cm²/s at a reactor power 20MW. Thermal neutron fluxes at the end of T1 and T2 guide tube were $1.2 \times 10^8$ n/cm²/s. Background dose rate is quite low in the beam hall, neutron dose rate was 6 µSv/h and gamma dose rate was 6 µSv/h at a reactor power of 20MW.

![Fig.1 General layout of the neutron guide tubes at the JRR-3M](image)

---

**Table 2 Characteristics of the neutron guide tubes at the JRR-3M**

<table>
<thead>
<tr>
<th>Guide tube</th>
<th>Characteristic wavelength (Å)</th>
<th>Beam cross-section (mm²)</th>
<th>Radius of curvature (m)</th>
<th>Length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>2</td>
<td>20 x 200</td>
<td>3.337.4</td>
<td>59.91</td>
</tr>
<tr>
<td>T2</td>
<td>2</td>
<td>20 x 200</td>
<td>3.337.4</td>
<td>58.98</td>
</tr>
<tr>
<td>C1</td>
<td>4</td>
<td>20 x 120</td>
<td>834.3</td>
<td>30.75</td>
</tr>
<tr>
<td>C2</td>
<td>4</td>
<td>20 x 120</td>
<td>834.3</td>
<td>51.08</td>
</tr>
<tr>
<td>C3</td>
<td>6</td>
<td>20 x 120</td>
<td>370.8</td>
<td>31.38</td>
</tr>
</tbody>
</table>

---

**DESIGN OF MEDICAL IRRADIATION FACILITY USING SUPERMIRROR GUIDE TUBE**

Thermal neutron flux at the end of JRR-3M neutron guide tube, is one tenth of the value ($1 \times 10^9$ n/cm²/s) requested by BNCT. Beam cross-section of the thermal guide tube is less than the requested value. We have designed a medical irradiation facility using a supermirror guide tube in the beam hall at the JRR-3M. Supermirror\cite{14} has a critical angle of total reflection two or three times larger than that of natural nickel mirror, so it can increase thermal neutron flux at the end of guide tubes. The outline of the proposed medical irradiation facility is as follows. The medical irradiation facility installed in the shielding room, consists of a supermirror guide tube, movable nickel guide elements and a beam shutter. Existing nickel guide tube (T-1 guide) in the biological shielding, the guide tunnel and the shielding room, is replaced by Ni/Ti supermirror guide tube. The radius of curvature is $3.337m$ as same as that of the existing nickel guide tube. Motor-operated three nickel guide elements are set between

---

---
the supermirror guide tube and the nickel one in the shielding room. Medical irradiation space is set after moving these elements (about 3m x 3m), it is wide enough for a patient lying down on a bed, working space and setting surgical instruments. The movable elements can transport neutrons to the neutron facilities at the beam hall, if medical irradiation is not done. Schematic view of a medical irradiation facility for BNCT is shown in Fig.2.

The supermirror guide tube is divided into three channels of 2mm width by glass substrate of 0.5mm width. The total neutron beam cross-section is 70mm x 200mm which meets the requested value. The supermirror consists of 125 layers of nickel and titanium layer with reflectivity of greater than 0.9.15

Background dose is quite low at the shielding room. Gamma dose rate measured just by the side of existing nickel guide tube at the shielding room was 350 μSv/h at a reactor power of 20MW. Neutron dose rate was 10 μSv/h. Capture gamma rays radiated from hydrogen and nitrogen in patient's body, is shielded by the concrete wall which is 80 cm thick of the shielding room. Patient's dose is controlled by existing beam shutter under stady reactor operation. A exposure treatment room is able to be set in the beam hall, where surgical operation can be done. It has a easy way of approach to irradiation room.

A neutron transmission and space distribution in the supermirror guide tube have been evaluated by using the "NEUGT" code,16 which were developed to calculate neutron transmission for the design assessment of the neutron guide tubes at the JRR-3M. The calculation showed good agreement with the experiment data of a neutron transmission and a neutron space distribution in the guide tubes.13 This neutron transmission analysis was done in the case of no abutment error. Reflectivity of supermirror is assumed to be 0.9. Thermal neutron flux at this irradiation field is expected to be $1.4 \times 10^9$ n/cm²/s. Table 3 shows the comparison of main characteristics on the medical irradiation facilities between new facility at the JRR-3 and the existing one at the JRR-2.

<table>
<thead>
<tr>
<th>Item</th>
<th>JRR-3M</th>
<th>JRR-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal neutron flux [n/cm²/s]</td>
<td>$1.4 \times 10^9$</td>
<td>$1.0 \times 10^9$</td>
</tr>
<tr>
<td>Neutron beam size [mm²]</td>
<td>70 x 200</td>
<td>500 x 500</td>
</tr>
<tr>
<td>Gamma dose rate [μSv/h]</td>
<td>350</td>
<td>500,000</td>
</tr>
</tbody>
</table>

CONCLUSIONS

"Pure" thermal neutron field for BNCT treatment has been designed by replacing the nickel guide tube with a supermirror guide tube at the JRR-3M. The characteristics of this facility such as neutron flux, beam size and background, meet the requirements for successful BNCT treatment. A treatment room is able to be set in the beam hall, where surgical operation can be done. It has an easy way of approach to irradiation room. It would be a most suitable medical irradiation field for BNCT treatment.
REFERENCES

1. G. L. Locher : Biological effects and therapeutic possibilities of neutron, Am. J. Roentgenol. Radium Therapy, 36, 1-13, 1936
4. K. Kanda, et al. : Elimination of gamma rays from a thermal neutron field for medical and biological irradiation purposes, Biological Dosimetry, IAEA, Vienna, 205
14. F. Mezei, Nobel polarized neutron devices : supermirror and spin component amplifier, Commu. on phys. 1, 81-85, 1976
PROGRESS IN STUDY OF A MEDICAL REACTOR FOR BORON NEUTRON CAPTURE THERAPY

Makoto SASAKI, Jitsuya HIROTA, Shigeo TAMAO, Keiji KANDA and Yutaka MISHIMA

Mitsubishi Atomic Power Industries, Inc.
4-1 Shibakouen 2-chome, Minato-ku, Tokyo 105, Japan

Mitsubishi Heavy Industries, Ltd.
4-1 Shibakouen 2-chome, Minato-ku, Tokyo 105, Japan

Research Reactor Institute, Kyoto Univ.
Noda, Kunatori-cho, Sennan-gun, Osaka 590-04, Japan

Kobe Univ. School of Medicine
Special Institute of Cancer Neutron Capture Therapy
7-5-1 Kusunoki-cho, Chuo-ku, Kobe 650, Japan
Present Address: MISHIMA Institute for Dermatological Research
3-17-8-801 Motonachi-dori, Chuo-ku, Kobe 650, Japan

ABSTRACT

A design study of a medical reactor for Boron Neutron Capture Therapy has made progress. Main specifications of the reactor are as follows; thermal power of 2 MW, water cooling by natural convection, semitight core of hexagonal lattice, UO₂ fuel rod of 9.5 mm diameter and no refueling in the reactor-life. Three horizontal and one vertical neutron beam holes are to be provided for simultaneous treatments by thermal and epithermal neutrons and for further biomedical research. The design objectives for the beam holes are to deliver the therapeutic doses in a modest time (30 to 60 min) with minimal fast neutron and gamma contaminants. The n-γ coupling Sn transport calculations have been carried out using n-21 and γ-9 group cross sections on 2-dim. practical models. The calculated results indicate that the design objectives will be achievable even if the thermal power of the reactor is reduced to 1 MW.

INTRODUCTION

A design study of a medical reactor has been carried out since July, 1988, with the cooperation of Kobe Univ., Kyoto Univ., Mitsubishi Heavy Industries, Ltd., Mitsubishi Atomic Power Industries, Inc. and others. It is intended in this study to survey and investigate the reactor concepts suitable for Boron Neutron Capture Therapy (BNCT) and to set up the main specifications of the reactor which is to be used exclusively for the treatment of cancers as well as for the further biomedical research.

At present, the clinical treatment by BNCT is being carried out only in Japan and many patients want the treatment including those in Europe, U.S.A. and Australia. The treatment by BNCT is applied to brain tumors and malignant melanomas, and good clinical results are achieved by a single radiation regimen. Brain tumor treatment was initiated in 1968 by Prof. H. Hatanaka of Teikyo Univ. and the number of treatments reaches 120 cases.
Recently Kyoto Univ. and other hospitals have started treatment. Malignant melanoma treatment was initiated in 1987 by Prof. Y. Mishima and Assist. Prof. M. Ichihashi (at that time) of Kobe Univ. The total number of these treatments by BNCT reaches 150 cases.

It is generally accepted that the optimum neutron source for BNCT is a small reactor. However, currently available research reactors such as Musashi Reactor, KUR and JRR-2 are not constructed exclusively for medical use, but rather as multi-purpose reactors. Since the thermal neutron flux available at the beam port is not so high, the time needed for the treatment is usually rather long. Further, the time available for medical use is limited because the research reactor is used for different purposes and the schedule is tight.

Studies of BNCT by epithermal neutrons are in progress in Europe, U.S.A. and Australia. Thermal neutron flux decays rapidly in the human tissue. If epithermal neutrons are utilized, it may be possible to treat various deep-seated cancers without surgery. It is important and necessary, however, to sufficiently suppress the fast neutron contamination in the therapeutic neutron beam.

In FY 1978-79, a design study of a neutron irradiation facility for BNCT was carried out under the support of the Ministry of Education, Science and Culture. In the study, the configuration of the neutron filter which delivers thermal or epithermal neutrons from a TRIGA reactor was investigated. A neutronics design of a medical therapy reactor was presented from INEL at the 1988 Int. Reactor Physics Conf. It addresses the feasibility of utilizing existing reactor technologies to deliver therapeutic doses by epithermal neutrons. The two primary fuel candidates are a 10 wt% $^{239}$U enriched UO$_2$ fuel and a 20 wt% $^{235}$U enriched UZrH fuel.

**CORE CONFIGURATION AND ANALYSIS**

Principal requirements for the design of the medical reactor in this study are as follows:

(1) The reactor is to be used exclusively for medical purposes.
(2) 50,000 patients are able to be treated or diagnosed in the reactor-life without refueling.
(3) The thermal power is less than 2 MW.
(4) The core is cooled by natural convection.
(5) Thermal and epithermal neutron beam holes are provided separately.
(6) No heavy water is used in the core.
(7) Existing proven reactor technologies are to be utilized.

A survey of characteristics of research reactors and small reactors in the world was carried out. In reference to the principal requirements, light water cooled and moderated PWR-type (oxide fueled) and TRIGA-type (hydride fueled) reactors seemed suitable for the medical reactor. Analyses of the core characteristics of these two reactors indicated that the oxide fueled core would be more feasible to the medical reactor because of the higher epithermal neutron flux availability and the less excess reactivity requirement. Furthermore, it will be possible to fabricate and reprocess the oxide fuel in Japan which is different from the case of the hydride fuel.

A harder neutron spectrum of the core is preferable in view of the availability of epithermal neutrons. A too tight core, however, results in an excessive increase of the fuel enrichment and a decrease of the control rod worth. Therefore, a semitight core is preferable. The average linear heat rate in the core is selected to be 20 W/cm. The characteristics of the core were examined for the optimization of the core parameters such as the volume ratio of moderator to fuel pellet (Vm/Vp), ratio of core height to
diameter and fuel enrichment.

The control rod worth was calculated and it was confirmed that seven control rods of cluster-type would be able to shut down the reactor safely under the condition of one rod stuck. It was also confirmed that the local boiling would not occur in the core even if the reactor power was raised ramp-wise from zero to the normal power in 5 min.

The main specifications of the core and fuel are given in Table 1 and the horizontal cross section of the core is shown in Fig.1.

Table 1. Main specifications of the core and fuel

| Thermal power | 2 MW |
| Active core height | 62 cm |
| Equiv. core radius | 25.5 cm |
| Vm/Vp | 1.0 |
| Fuel | UO₂ (~0.5 t) |
| ²³⁵U enrichment | 4 wt% |
| Cladding outer dia. | 9.5 mm |
| Assembly pitch | 112 mm |
| Pin pitch | 11.4 mm |
| Lattice geometry | Hexagonal |
| No. of fuel rod | 91/ass'y |
| No. of fuel ass'y | 19 |

Fig.1. Horizontal cross section of the core

<table>
<thead>
<tr>
<th>Core</th>
<th>Bi</th>
<th>Al</th>
<th>D₂O</th>
<th>Bi</th>
<th>Air</th>
<th>Rossi liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>25.5</td>
<td>46.0</td>
<td>66.0</td>
<td>136.0</td>
<td>L_{146.0}</td>
<td>217.0</td>
</tr>
</tbody>
</table>

(a) Horizontal thermal neutron beam hole

<table>
<thead>
<tr>
<th>Core</th>
<th>Bi</th>
<th>Al</th>
<th>D₂O</th>
<th>Bi</th>
<th>Air</th>
<th>Rossi liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>25.5</td>
<td>46.0</td>
<td>137.0</td>
<td>217.0</td>
<td>237.0</td>
<td></td>
</tr>
</tbody>
</table>

(b) Horizontal epithermal neutron beam hole

<table>
<thead>
<tr>
<th>Core</th>
<th>Bi</th>
<th>Al</th>
<th>D₂O</th>
<th>Bi</th>
<th>Air</th>
<th>Rossi liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>31.0</td>
<td>39.0</td>
<td>70.4</td>
<td>119.0</td>
<td>L_{134.0}</td>
<td>194.0</td>
</tr>
</tbody>
</table>

(c) Vertical thermal neutron beam hole

<table>
<thead>
<tr>
<th>Core</th>
<th>Bi</th>
<th>Al</th>
<th>D₂O</th>
<th>Bi</th>
<th>Air</th>
<th>Rossi liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>70.4</td>
<td>120.0</td>
<td>135.0</td>
<td>194.0</td>
<td>214.0</td>
<td></td>
</tr>
</tbody>
</table>

(d) Vertical epithermal neutron beam hole

Fig.2. Reference slab models of the neutron beam holes (in unit of cm)
NEUTRON FILTER CONFIGURATION AND ANALYSIS

Three horizontal neutron beam ports are to be provided for simultaneous treatments and advanced research. Therapeutic doses of thermal or epithermal neutrons are also available at a vertical neutron beam port by using a rotating plug. In order to examine the neutron filter composition and to optimize the neutron filter configuration, 1-dim. n-γ coupling Sn transport calculations were carried out using JSSTD-100N/40G-J35. The reference slab models of the neutron beam holes are shown in Fig.2.

The neutron filter for epithermal neutrons which consists of aluminum and heavy water was first proposed by Y. Oka, et al14. Aluminum is an unique material whose cross sections for fast neutrons are larger than those for epithermal neutrons. Bi is used for the gamma shielding. LiF or Cd is used to cut off thermal neutrons. The effect of the (γ, n) reaction of heavy water is taken into account by Aoki's method8). The fast neutron and gamma dose due to the fast neutron and gamma contaminant are calculated using the conversion coefficients9,17). In this study, the thermal, epithermal, and fast neutrons are denoted as the neutrons less than 1 eV, between 1 eV and 1 KeV, and more than 1 KeV, respectively.

The Sn transport calculations of the neutron flux (n/cm²·s), neutron dose rate (Gy/h) and gamma dose rate (Gy/h) were carried out on several 1-dim. models which were different from the reference model. The effect of the (γ, n) reaction of heavy water can be estimated from the decrease of the fast neutron dose rate by the neglect of the reaction. The gamma dose rate due to the gamma contaminant is equal to the dose rate obtained on the model without the Rossi liquid for tissue simulation. The calculations indicate that the (n, γ) reaction in the tissue contributes to more than 90 % of the gamma dose rate.

As for the horizontal thermal and epithermal neutron beam hole, the calculated results indicate that the reference model is almost the best choice for each. As for the vertical thermal and epithermal neutron beam hole, the existence of the cooling water region tends to decrease the neutron flux available at the beam port. Since the total length of the beam hole is designed to be shorter than that of the horizontal beam hole as seen in Fig.2, the neutron flux available at the beam port is almost equal to that available at the horizontal beam hole. However, the fast neutron and gamma dose rate tend to be larger than those at the horizontal beam port. The horizontal and vertical beam hole provided around the core are shown in Fig.3. A rotating beam shutter is provided for each beam hole to shut the neutron beam in emergency. Each irradiation room is 4 m wide to facilitate the neutron irradiation of the patient.

![Fig.3 Conceptual drawing of the beam holes](image-url)
EVALUATION OF CHARACTERISTICS OF THE NEUTRON BEAM HOLE

The design objectives for the neutron beam hole are given as the values at the beam port as follows:

(1) Thermal neutron flux; $1.2 \times 10^{13}$ n/cm$^2$ in 30 to 60 min.
(2) Epithermal neutron flux; $0.6 \times 10^{13}$ n/cm$^2$ in 30 to 60 min.
(3) Fast neutron dose during the treatment; less than 2 Gy.
(4) Gamma contaminant dose during the treatment; less than 1 Gy.

---

**Fig. 4.** Contour map of the thermal neutron flux in the horizontal thermal neutron beam hole (in unit of n/cm$^2$.s)

---

**Fig. 5.** Contour map of the epithermal neutron flux in the vertical epithermal neutron beam hole (in unit of n/cm$^2$.s)
In order to evaluate the thermal and epithermal neutron flux, fast neutron dose rate and gamma dose rate in the horizontal and vertical beam holes, 2-dim. n-\gamma coupling Sn transport calculations have been carried out using n-21 and \gamma-9 group cross sections and neglecting the (\gamma,n) reaction of heavy water. Fig.4 and 5 show the contour map of the thermal neutron flux in the horizontal thermal neutron beam hole and the epithermal neutron flux in the vertical epithermal neutron beam hole. Fig.6 and 7 show the neutron spectra in the horizontal thermal and vertical epithermal neutron beam hole. Table 2 summarizes the characteristics at the horizontal and vertical neutron beam ports. In this table, the effects of the (\gamma,n) reaction of

![Graph](image1)

**Fig.6. Neutron spectra in the horizontal thermal neutron beam hole**

![Graph](image2)

**Fig.7. Neutron spectra in the vertical epithermal neutron beam hole**
heavy water and the \((n, \gamma)\) reaction of Rossi liquid are taken into account by using the 1-dim. results.

Table 2. Summary of the characteristics at the neutron beam ports

<table>
<thead>
<tr>
<th></th>
<th>Horizontal beam hole</th>
<th>Vertical beam hole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermal</td>
<td>Epithermal</td>
</tr>
<tr>
<td>Neutron flux ((10^{10} \text{ n/cm}^2\cdot\text{s}))</td>
<td>1.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Treatment time (min)</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>Fast neutron dose (Gy)</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Gamma contaminant dose (Gy)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The table shows the progress made since the previous presentations; the characteristics of the horizontal thermal neutron beam hole have been improved and the design objectives have been achieved for the vertical neutron beam hole. There will be large enough margin for the addition of a shield or collimator to the patient, or for the further reduction of the fast neutron contaminant, because the time needed for the treatment is much shorter than the design objective. It may be possible to achieve the design objectives even if the reactor power is reduced from 2 MW to 1 MW.

LAYOUT INSIDE OF THE REACTOR BUILDING

Fig.8 shows the first floor layout inside of the reactor building. There are three irradiation rooms and one neutron guide tube room provided for in vivo measurement of the \(^{10}B\) concentration in tumor cells. A patient on the bed is sent from the preparation room to the irradiation room. In the

Fig.8. First floor layout inside of the reactor building
measurement room, measurements of gold foil and TLDs irradiated with the patient are carried out to monitor the neutron and gamma flux.

CONCLUSION

The design study of the medical reactor for BNCT has made progress. This reactor concept utilizes only existing proven reactor technologies, and the refueling will be unnecessary for the medical use of 30 years. The special features of the medical reactor are the availability of epithermal neutrons and provision of the vertical neutron beam hole. The 2-dim. n-γ coupling Sn transport calculations indicate that the reactor will be able to deliver the therapeutic doses in about 15 min with the fast neutron dose less than 2 Gy and gamma contaminant dose less than 1 Gy. The design objectives for the neutron beam hole may be achievable even if the thermal power of the reactor is reduced from 2 MW to 1 MW.

ACKNOWLEDGEMENTS

This work is performed as the cooperative research (principal investigator: Prof. Y. Mishima, M.D., Ph.D.) under Grant-in-Aid of the Ministry of Education, Science and Culture, Japan for FY 1988-92.

The authors would like to express their thanks to all the participants of the study group, including Professors M. Ichihashi of Kobe Univ., H. Fukuda of Tohoku Univ. and O. Aizawa of Musashi Inst. of Tech. AERL, and Lec. T. Kobayashi of Kyoto Univ. RRI, for useful discussions, and to Dr. A. Hasegawa of JAERI for the preparation of the JSSTDL Library. They also wish to thank Mrs. T. Ito of Computer Software Development Co. Ltd. and Messrs. M. Hayano, T. Kato and Y. Hasegawa of MAPI for the cooperation in this work.

REFERENCES

7) ICRP Publication 21, Table 4 (1973)
NEUTRON DIFFRACTION TOPOGRAPHIC OBSERVATION OF NI-BASE SUPERALLOY SINGLE CRYSTALS

*Hiroshi TOMIMITSU, *Kazuya AIZAWA, *Katsumi IIJIMA and *Akira YOSHINARI

*Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

*2nd Material Department
Hitachi Research Laboratory, Hitachi Ltd.
Ohmika-cho, Hitachi-shi, Ibaraki-ken, 319-12 Japan

ABSTRACT

In order to develop the high quality gas turbine, the neutron diffraction topography (NDT) was applied to the characterization of the turbine blade made of the Ni-base superalloy single crystals grown by "bypass" method. NDT-observation was carried out with a conventional double-axis goniometer at the PNO in JRR-3M. The followings were preliminarily revealed. 1) The so-called "substructure" was observed clearly within the specimen. 2) Every rocking curve showed more or less asymmetry and the FWHM of around 1°. The angular incoherency of around 1° was observed at the recombining part of the main part and the bypassed branch. 3) Every rocking curve showed a small "shoulder" in the higher angular region, giving the topographs very similar to that by main peak. 4) All angular amount in the above mentioned facts were much reduced by the observation with the neutron beam of shorter wavelength.

INTRODUCTION

It is a very important problem in Japan to develop the heavy duty gas-turbine blade for the future generation of electricity. Through several national research projects in Japan, Ni-base superalloy single crystal, i.e., TMS12, seems to be one of the most promising solution for the above\(^1\). To characterize them and to contribute to the development of the high quality turbine blade is the main theme of the present investigation.

For its highest penetrating power of neutron in almost all materials, and with the similar mechanism to the conventional X-ray diffraction topography and the electron microscopy (the dark field method), the neutron diffraction topography (NDT) is very powerful for the direct observation of metallic crystals as demonstrated by one of the present authors (HT) in the case of Cu-5%Ge single crystals\(^2\).

In the present study, the NDT was applied to the characterization of the Ni-base superalloy single crystals grown by "bypass" method into a shape of turbine-blade, and several preliminary results will be given.

SPECIMEN

A single crystal of Ni-base superalloy called TMS-12, the composition being 73.3%-Ni, 8.0%-Cr, 4.4%-W, 11.7%-Al and 2.6%-Ta in atomic ratio, was grown into a [001] direction by so-called bypass-method into a rather complicated form as the prototypical turbine blade.
having internal cooling-water-paths and external cooling-fins. From the turbine blade, a plate of 3mm thickness was sliced. Further, two kinds of specimen were cut out from the slice for the observation, A) the specimen containing the branching part from the main part near the growth-originating position, and B) the specimen containing the recombining part of the bypass branch to the main part. All situations mentioned above are illustrated in Fig. 1, where the growth direction is shown by the arrow and the crystallographic orientations and the scale mark are shown.

![Diagram of turbine blade and specimen cutouts](image)

**Fig. 1. Photograph of the Prototypal Turbine Blade (Left) and the Schematic Drawing of the Central Section of the Blade (Right) and Specimen cut out of the Slice.**

From the sliced plate of 3mm thickness cut out from the turbine blade, two kinds of specimen were cut out for the observation, A) the specimen containing the branching part from the main part, and B) the specimen containing the recombining part of the bypass branch to the main part.

### NDT EXPERIMENT

The neutron experiments were carried out with the PNO (Precise Neutron Optics) apparatus settled at the 3G beam hole in the JRR-3M. The experimental arrangements are illustrated in Fig. 2, where C means the beam-shutter and collimator exchanging system of 2.5', 10' and 30' collimators, M the so-called "double-monochromator" system of PG-crystals, IS the incidence slit, S the specimen crystal, P the photographic cassette, D the \(^3\)He detector and T the constant-temperature chamber of around 3×3×3m\(^3\). The subscripts + or - in P and D mean the (+,+), (+,-) setting of the specimen crystal in relation to the second monochromator crystal. The walls of the constant-temperature chamber are also effective for the noise-shielding. IS, S, P and D are set on a conventional goniometer, which has two rotating axes, one for specimen and another for detector, with the encoder system of the minimum reading of 0.001° for every axis. They are all set on a vibration-free table in the
more precisely temperature-regulated chamber of $1.3 \times 2.3 \times 2.0 \text{m}^3$. The Soller type beam collimator C with the angular divergence of 2.5° was used throughout the present experiment. The neutrons of the wavelengths of 2.5Å and 1.8Å were selected by the +,- successive reflection with the PG-double crystals of the nominal mosaic-spread of 0.4°. Sometime, their secondary order reflections, i.e., 1.25Å and 0.9Å, were used and the results were compared with them by other wavelengths. Every topograph was recorded on a high quality Kodak dental X-ray film with a Gd-foil as the (n,γ) converter attached behind the film in an Al-cassette, the resultant spacial-resolving power was estimated to be around 20–30μm.

Fig. 2. Experimental Arrangement with the PNO Apparatus at JRR-3M.

C is the beam-shutter / collimator exchanging system, M the "double-monochromator" system with PG-crystals, IS the incidence slit, S the specimen crystal, P the photographic cassette, D the 3He detector and T the temperature-regulated chamber. The subscripts + or - in P and D mean the (+,+), (−,+), (+,−), or (−,−) setting of the specimen crystal in the relation to the second monochromator crystal. IS, S, P and D are set on a conventional double-axis goniometer. Topographs were recorded on a high quality dental X-ray film with a Gd-foil as the (n,γ) converter attached behind the film in an Al-cassette.

EXPERIMENTAL RESULTS

The specimens were examined with several diffraction techniques, such as with the so-called θ–2θ measurements, giving the lattice constant, with the one-round rotation of the specimen crystal with the detector fixed to a 2θ position, giving the extra reflection if exited, and with normal rocking curve measurement, giving finer structure of a certain reflection. Fig. 3(a) is an example of the θ–2θ measurement of the specimen (A), the full angular range of the abscissa being 200°, where the specimen crystal was rotated synchronously with the detector from the (−), (200) or the 200 reflecting position to the (−), (200) or the 200 reflecting position. From the angular deviation between the peaks A and D, both being 200 reflection by 2.5Å, the lattice constant of the presentages specimen was roughly estimated to be around 3.64Å, which is several percentages larger than expected from the pure Ni crystal. Similar value was obtained from the deviation between the peaks B and C, both being also the 200 reflection but by 1.25Å.

Figs. (b) and (c) are the "enlargement" of the individual reflection peaks A and D in (a), the full angular range of the abscissa being 3°, where (b) is reversed in the abscissa so as to be compared directly with (c). In both curves, it is clearly seen that (1) the full width at half maximum (FWHM) is around 1°, (2) a shoulder or a subpeak deviated around 1° from the main peak position is seen in their higher-angle region and (3) the angular quantities above
were reduced almost half in the curves by the half-wavelength. Those facts mentioned above were almost commonly observed in the specimens A and B.

Fig. 3. Example of θ–2θ Measurement Curve from 220 (Left) to $\bar{2}$20 Reflection (Right) by 2.5Å. (a) shows the total range of the measurement with the angular range of 200° (abscissa), while (b) and (c) are the "enlargement" of the individual peaks A and D in (a) with the angular range of 3°, where (b) is reversed in the abscissa, see text.

Fig. 4 is the neutron diffraction topograph of the specimen A containing the branching part, taken with $\bar{2}$00 reflection by 2.5Å giving the $\bar{1}$10 projection of the specimen crystal. Apparently, the vertical linear images are dominant, indicating a certain substructure within the crystal parallel to the macroscopic growth-direction, the spacing of the neighboring linear images being measured around 0.5mm.

Fig. 4. NDT of the Specimen A.
It is taken with $\bar{2}$00 reflection by 2.5Å, clearly showing the vertically arrayed linear images nearly parallel to the growth direction. Incidence slit of 5mm width was used.

Fig. 5(a) is a rocking curve of the specimen (B) taken with 022 reflection by
1.8 Å. It is clearly seen that there is also a subpeak in the higher-angle region, apart around 1° from the main peak. Figs. 5(b)~(f) are the topographs taken at the various angular positions as indicated by A, B, C, D, and E in (a), all of them being the 001 projections. It is clearly seen that (1) there exist a clear boundary between the branch part (Left) and the main part (Right) in every topograph, the boundary existing at almost the edge of the main part, (2) the branch part is taken just on-Bragg with the main peak (d), showing horizontal linear images, while the main part is taken just on-Bragg with the subpeak position (f), showing rather two-dimensional images, furthermore (3) almost similar images are taken for the branch part and the main part with other angular positions deviated from the main peak position.

Fig. 5. The Rocking Curve (a) and the Topographs (b)~(f) of the Specimen (B).

Topographs were taken at various angular positions indicated by A, B, C, D, and E in (a) with 022 reflection by 1.8 Å, all topographs giving the 001 projections. The full angular range of the rocking curve (a) is 3°. The recombining position is clearly seen at almost central position in each topographs. The images in left hand side meaning the branch part, showing horizontal linear images, while the images in the right hand side mean the main part, showing two-dimensional images. Incidence slit of 1 mm width was used.
DISCUSSION

The substructure was suggested in the present crystal, which was rather similar to that observed in the Cu-5%Ge single crystal\(^2\), and also suggested the \(<100>\) dendritic growth along vertical in the main part and horizontal in the branch part. This seems to be caused by the locally dominant temperature-gradient. In the recombination of the branch part to the main part, angular misfit up to 1° was detected and the recombining position was revealed much nearer to the main part than expected, which might be caused by the fact that the heat capacity in the branch part with much smaller cross section was smaller than that of the main part, and, accordingly, the growth rate of the branch part was much larger than that of the main part. In the bypass method, it seems, thus, very important to control the temperature-gradient in the branch part just as the main part, in order to keep the orientation and the growth rate the same to that at the main part.

Further investigation is necessary to ensure the certainty and the dependence on the wavelength of the angular quantities observed in the present experiments, such as the lattice constants of several percentages larger than expected, the FWHM of the rocking curve and the deviation of the main peak and the subpeak.

CONCLUSION

The NDT was rather successfully applied to the direct observation of a single crystal of Ni-based superalloy, in connection with several diffraction techniques, giving the preliminary results as following:
(1) The present crystal is a "single crystal" of FCC with the lattice constants of around 3.64Å.
(2) In every topograph, it showed \(<100>\) linear images of 0.5mm intervals suggesting a kind of substructure, parallel to the locally dominant temperature-gradient.
(3) In the main part, the linear image is parallel to [001], and the FWHM of the reflection curve become broader as the crystal grows.
(4) In the branch part, the crystallographic properties seem to be almost the same as the main part, but when it connects to the main part, the linear image is parallel to [100], and the angular misfit is around 1°.
(5) The recombining position of the branch to the main part was much nearer to the main part rather than the middle point, that was the scheduled and expected position.
(6) The angular quantities such as FWHM and deviation between main peak and shoulder or subpeak varied when the wavelength used was changed.

REFERENCES

1) On Ni-base superalloy, for example;
2) On NDT and on the observation of Cu-5%Ge single crystal, for example;
DIFFRACTION PLANE DEPENDENCY OF ELASTIC CONSTANTS IN FERRITIC STEEL IN NEUTRON STRESS MEASUREMENT

M. HAYASHI, M. ISHIWATA, N. MINAKAWA and S. FUNAHASHI

Mechanical Engineering Research Laboratory, Hitachi, Ltd.
1-1, Saiwaicho 3-chome, Hitachi-shi, Ibaraki-ken, 317 Japan

Hitachi Works, Hitachi, Ltd.
1-1, Saiwaicho 3-chome, Hitachi-shi, Ibaraki-ken, 317 Japan

Department of Physics
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

Neutron diffraction measurements have been made to investigate the elastic properties of the ferritic steel obtained from socket welds. The Kroner elastic model is found to account for the [hkl]-dependence of Young’s modulus and Poisson’s ratio in the material. Maps of residual stress are later to be made by measuring lattice strain from shifts in the (112) diffraction peak, for which the diffraction elastic constants are herein found to be $E=243\pm5$ GPa and $\nu=0.28\pm0.01$.

INTRODUCTION

Neutron diffraction is the only method available to determine non-destructively the residual stresses inside weldments. Thermal neutron are generated inside a nuclear reactor, and are emitted through beam tubes to be diffracted from a squeezed, single-crystal monochromator. The diffracted neutrons have a characteristic wavelength, $\lambda$, typically between 0.13nm and 0.26nm. They are shaped into a rectangular beam by masks made of neutron absorbing cadmium. The cross sectional area of the beam is chosen to match the desired spatial resolution in a specimen. Neutrons are scattered from the incident beam direction through angles, $2\theta$, according to Bragg’s law,

$$\lambda=2d(hkl)\sin(\theta),$$  (1)

where $d(hkl)$ is the spacing between atomic planes with Miller indices $(hkl)$.

With a neutron diffractometer, the intensity of diffracted neutrons is measured as function of scattering angle. By fitting the raw neutron data with a gaussian function plus a sloping background, the mean scattering angle of each diffraction peak can be determined to a typical precision of $\pm0.003^\circ$. The neutron wavelength can also be determined to a high precision, $\pm1\times10^{-9}$ nm, by calibration against a standard silicon powder specimen, obtained from the National Institute of Standards and Technology (NIST). Hence, values of $d_{hkl}$ can be determined to a precision better than 1 part in $10^5$. Comparing the value of $d(hkl)$ at a location in a weldment with the value, $d_o(hkl)$, in a stress-free sample, provides a
direct measurement of strain, \( \varepsilon \) (hkl), in the atomic lattice,

\[
\varepsilon \text{ (hkl)} = \frac{(d \text{ (hkl)})}{d_0 \text{ (hkl)}} - 1.
\]  

(2)

The strain is determined in the specimen direction that is parallel to the bisector of the incident and diffracted neutron beams. The principal components of strain are therefore obtained by choosing appropriate specimen orientations.

Assuming that the radial (R), axial (A) and hoop (H) directions are the principal axes of the stress field in a welded tube, and that the material can be treated as a homogeneous elastic continuum, the principal components of residual stress, \( \sigma \), can be calculated directly from the algebraic expression,

\[
\sigma = \frac{E}{(1 + \nu)} \left[ \varepsilon_R + \frac{\nu}{(1 - 2\nu)} \left[ \varepsilon_R + \varepsilon_A + \varepsilon_H \right] \right]
\]  

(3)

where \( E \) is Young’s modulus, \( \nu \) is Poisson’s ratio and the radial, axial and hoop components of stress, \( \sigma_R \), \( \sigma_A \) and \( \sigma_H \), respectively, are obtained by cyclic permutation of the indices in Eq. (3).

When diffraction provides the original data on lattice strains, the elastic constants, \( E \) and \( \nu \), which appear in Eq. (3) must account for a dependence of elastic properties with direction, [hkl], in a single crystal. A given stress applied in the elastically-soft [200] direction of a single crystal of iron would produce a much larger strain than if it was applied in the elastically-stiff [222] direction. Crystallites embedded in a matrix of polycrystalline material also exhibit an [hkl]-dependence in their elastic response to an applied load. Therefore, to calculate stress from diffraction-measured strains, [hkl]-dependent diffraction elastic constants must be determined. Diffraction elastic constants can be calculated from single-crystal elastic constants[1] by a program[2] based on the Kroner model of elasticity in a polycrystalline aggregate[3]. However, it is preferable to determine the diffraction elastic constants experimentally. This is achieved by applying known stresses to specimens of the materials in question and then measuring lattice strain by neutron diffraction from the same (hkl) planes with which the residual stress measurements will be made.

**EXPERIMENT**

A loading rig was custom-built to fit onto the L3 neutron diffractometer, located at the NRU reactor at the Chalk River Laboratories of AECL Research, Canada. An interface was developed at chalk River to permit loads to be set automatically, controlled to within ±0.011kN and recorded by the neutron diffractometer’s data acquisition system. The rig had a maximum load of 50kN and could be operated with the load applied vertically (perpendicular to the scattering vector, for determining Poisson’s ratio), or horizontally (parallel to the scattering vector, for determining Young’s modulus). The load was set by a screw-driven cross-head, and read by a load cell with a calibration table that was traceable to the National Institute of Standards and Technology (NIST).

A specimen was machined from the base material of a socket weld pipe. The specimen had a cross-sectional area of 21.9 mm², and a gauge length of 50mm. Strain gauges were affixed to the surface of the gauge length to determine bulk-averaged values of Young’s modulus and Poisson’s ratio for
the material. Readings were taken at irregular intervals during the
course of neutron diffraction measurements of lattice strain.

The L3 neutron diffractometer was configured to produce a neutron
beam of wavelength 0.10984nm by diffraction from the (117) planes of a
squeezed single crystal germanium monochromator. Soller-slit collimators
in the incident and diffracted beams restricted the total angular
divergence in the scattering plane to be 0.45° and the total vertical
angular divergence to be about 3°. The spatial widths of the neutron
beams were restricted by masks to be approximately 25mm. After a given
load was set on the specimen, a single ¹⁹He-based neutron detector was
scanned through the (110), (200), (112), (220) and (222) diffraction
peaks in steps of 0.1°. Each set of five diffraction peaks was acquired
in about 3 hours. Strains were determined through Eqs. (1) and (2), taking
as stress-free references, d₀(110), d₀(200), d₀(112), d₀(220), and d₀(222),
the lattice spacings measured at zero load. Each lattice spacing was
related to the lattice constant, a, through the geometrical relationship
dₖₖₙ₁=a/√h²+k²+l². An average value of the stress-free lattice constant,
a=0.28664±0.00001nm, was obtained from measurements of the five lattice
spacings at zero load both in the series of measurements for Young’s
modulus and in the series of measurements for Poisson’s ratio. The typical
error in determining strain was ±0.8×10⁻⁴.

RESULTS AND ANALYSIS

The strain gauge readings are plotted in Fig.1, where it is clear
that both the Young’s modulus and Poisson’s ratio data are well-
represented by straight lines that have been fitted by least square method.
The resulting bulk elastic constants are E=222±10GPa and ν=0.28±0.02.

It is customary in neutron-diffraction strain analysis to choose (hkl)
peaks whose elastic properties are similar to those of the bulk material,
as measured by strain gauges. These peaks include the (110), (112) and
(220), all of whom are expected to exhibit equivalent elastic behaviour.
A comparison is made of strains determined by neutron diffraction from
the (110), (112) and (220) peaks in Fig.2. All of the data sets are well-
represented by a single straight line with slope 243±50Pa, nearly the
same value as obtained by the strain gauges. This line is denoted as the
(hhl) line and the strains obtained by averaging (110), (112) and (220)
data are denoted as (hhl) strains. A comparison of (hhl) strains and the
least-squares lines that fit the strain gauge data is shown in Fig.3 to
emphasize that the bulk strains determined by strain gauges are indeed
nearly equivalent to strains measured by neutron diffraction from the
(110), (112) or (220) peaks. Therefore, as is normally assumed, it is
reasonable to apply bulk elastic constants to convert (hhl) strains to
stresses through Eq.(3). However, measurements have now been made of the
true diffraction elastic constants for (hhl) peaks, E=243±50Pa and ν=
0.28±0.01. These measured values can be used in a future study of
residual stresses in socket-welds.

Three data sets, representing strains measured in the stiffest [222],
softest [200] and average [hhl] crystallographic directions, are plotted
together in Fig.4. Lines are fitted by the least square method to obtain
values of Young’s modulus that depend clearly on [hhl]. The dependence of
Young’s modulus on [hkl] is explained very well by the Kroner elastic
model calculation[2,3], as presented in Table I. The calculation begins
with the single crystal elastic constants for pure iron[1], C₁₁=230GPa,
$C_{44} = 135 \text{GPa}$ and $C_{44} = 117 \text{GPa}$. Young's modulus and Poisson's ratio are calculated for each (hkl) assuming that grains are spherical and the texture is random. The bulk values of Young's modulus and Poisson's ratio for pure iron are 211 GPa and 0.29, respectively[1]. These are slightly less than the bulk values determined by strain gauges in the socket weld material. Therefore the [hkl]-dependent Young's moduli that were calculated for pure iron have been scaled by the ratio of the bulk values of Young's modulus to give a prediction of the diffraction elastic constants in the socket weld pipe material. The predicted diffraction elastic constants and the [hkl]-dependent elastic constants determined by neutron diffraction always agree to within twice their standard errors. The Kroner elastic model is therefore confirmed as a valid method to obtain diffraction elastic constants in fine-grained, weakly-textured ferritic steel.

CONCLUSIONS

Strains determined from shifts in the angular positions of the (112) neutron diffraction peak are an excellent approximation to the strains that are measured by strain gauges on bulk material with the same applied stress. Residual stresses can be calculated from (112)-strains through Eq. (3) with the measured diffraction elastic constants, $E=243 \pm 5 \text{GPa}$ and $\nu = 0.28 \pm 0.01$. Even if measurements were not available, the diffraction elastic constants that are calculated by the Kroner method from a combination of single-crystal and bulk elastic constants in the literature are reliable for socket-weld ferritic steel.

REFERENCES


Table I. Comparison of the hkl-dependent elastic constants.

<table>
<thead>
<tr>
<th>BULK ELASTIC CONSTANTS</th>
<th>Pure Iron</th>
<th>Socket Weld Pipe Material (by strain Gauges)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's Modulus (GPa)</td>
<td>211</td>
<td>222</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.29</td>
<td>0.29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DIFFRACTION ELASTIC CONSTANTS</th>
<th>(hkl)</th>
<th>$\langle hh1 \rangle$</th>
<th>222</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated for Pure Iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young's Modulus (GPa)</td>
<td>174</td>
<td>224</td>
<td>248</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.33</td>
<td>0.28</td>
<td>0.25</td>
</tr>
<tr>
<td>Scaled by Bulk Values</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young's Modulus (GPa)</td>
<td>183</td>
<td>236</td>
<td>261</td>
</tr>
<tr>
<td>Neutron Diffraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Young's Modulus (GPa)</td>
<td>182</td>
<td>243</td>
<td>268</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>0.31</td>
<td>0.28</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Fig. 1 Measurements of Young’s modulus and Poisson’s ratio by strain gauges.

Fig. 2 Strains determined by neutron diffraction for (110), (112) and (220) planes.
Fig. 3 Comparison of averaged (hhl) strains obtained by neutron diffraction and least square fit of strain gauge data.

Fig. 4 Strains determined by neutron diffraction for elastically soft (200) and stiffest (222) planes.
X-RAY RESIDUAL STRESS MEASUREMENT AND ITS VARIATION DURING
PLANE BENDING FATIGUE AND SLIDING WEAR PROCESSES IN TiC, TiN,
TiB₂ AND Al₂O₃ CoATED CARBON STEELS

Takashi ENDOH, Kohji IDEMITSU and Mamoru KAWAKAMI

Department of Metallurgical Engineering
Tokai University
1117, Kitakaname, Hiratsuka, Kanagawa, 259-12
Japan

ABSTRACT

The development of ceramic coating to metals was stimu-
lated by the need for high temperature, wear and
Corrosion resistant materials. Recently TiC, TiN, TiB₂
and Al₂O₃ are used as ceramic coating materials.
In the present study, the X-ray method was successfu-
lly applied to measure the residual stress distribu-
tion in their ceramics coated steels. The X-ray elast-
ic constants were determined and compared with the
mechanically measured values. And plane bending and
sliding wear tests were carried out. The X-ray method
was successfully applied to measure the residual struc-
ture changes during fatigue and wear processes. The
relationship between the change of residual stress
and damage accumulation was investigated.

INTRODUCTION

Ceramic coating is utilized particularly for its refracto-
ry properties and wear resistance. One of the most important
needs in ceramic coating to metals is to compensate for thermal
expansion mismatch between coating film and substrate. By means
of this mismatch, residual stress distributes. It may be impor-
tant to make clear the effects of residual stress on various
fracture behaviors.

X-ray stress measurement can be considered to be the most
appropriate method for measuring residual stress in ceramics,
because it permits a rapid and nondestructive measurement in a
small area on the surface of polycrystalline materials. In this
method, the stress value is calculated selectively from strains
of a particular diffraction plane in the grains which are favo-
rously oriented for the diffraction. Therefore, the stress con-
tant and elastic constant for a particular diffraction plane
should be determined experimentally in order to measure the res-
idual stress accurately by X-ray diffraction. (1-7) And the X-ray
parameters are effective to detect the damage accumulation.
EXPERIMENTAL

Materials
The substrate materials were 0.45 mass% carbon steels. (JIS S45C) The bending specimens were processed mechanically. Ceramic coating processes were given in Tables 1 and 2. Ceramic coatings were conducted to both surfaces.

Elastic Constants and Residual Stress Measurement
Mechanical elastic constants of ceramic coating film were measured by using composite beam bending method. Residual stress was determined by the X-ray sin²ψ method. Tables 1 and 2 show the X-ray diffraction conditions. X-ray elastic constants were determined. Bending stress was applied to the specimen by using a small bending device. The valous elastic applied stress ($\sigma_M$) were measured with a strain gauge attached on the back side of the specimen. At the same time, the strain of the upper side of the specimen was measured by X-ray.

$$S_2/2 = (1+\nu)/E = (\cot\theta_0/2)\cdot \pi/180 \cdot (3\sigma_M/3\sigma_M)$$  \hspace{1cm} (1)

$$S_1 = -v/E = (\cot\theta_0/2)\cdot \pi/180 \cdot (\alpha(2\theta_\psi=0)/3\sigma_M)$$  \hspace{1cm} (2)

X-ray elastic constants $S_2/2$ and $S_1$ were obtained from Eqs. (1) and (2). Where, $M$ is a slope of 2θ - sin²ψ diagram and $2\theta_\psi=0$ is an intercept of 2θ - sin²ψ diagram.

$$K = -E/2(1+\nu)\cdot \cot\theta_0 \cdot \pi/180$$  \hspace{1cm} (3)

X-ray stress constant $K$ in Eq. (3) is calculated.

Plane Bending Fatigue and Sliding Wear Tests
Plane bending fatigue and Amerig type sliding wear tests were conducted, and the changes of residual stress during their processes were measured.

Table 1  Coating methods and X-ray diffraction conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>TiC</th>
<th>TiN</th>
<th>TiB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formed condition</td>
<td>CVD</td>
<td>PVD</td>
<td>CVD</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>fcc</td>
<td>fcc</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>a=4.528</td>
<td>a=4.240</td>
<td>a=3.028, c=3.228</td>
</tr>
<tr>
<td>Characteristic X-ray</td>
<td>Co-Kα</td>
<td>Co-Kα</td>
<td>Co-Kα</td>
</tr>
<tr>
<td>Diffraction plane</td>
<td>(113), 2θ=121.79°</td>
<td>(420), 2θ=141.54°</td>
<td>(221), 2θ=141.58°</td>
</tr>
<tr>
<td>Tube voltage (kV)</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube current (mA)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector</td>
<td>Scintillation counter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated area (mm²)</td>
<td>5x10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed time (sec)</td>
<td>15</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>Step width (deg)</td>
<td>0.10</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>Incident beam angle (deg)</td>
<td>-10, -5, 0, 5, 10, 15, 30</td>
<td>0.10, 0.20, 0.30, 0.40</td>
<td>-24, -14, -6, 6</td>
</tr>
<tr>
<td>Facility</td>
<td>○</td>
<td>△</td>
<td>○</td>
</tr>
</tbody>
</table>
### Table 2 Coating methods and X-ray diffraction conditions.

<table>
<thead>
<tr>
<th>Material</th>
<th>Al₂O₃</th>
<th>ZrO₂</th>
<th>ZrN</th>
<th>HfN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formed Condition</td>
<td>Plasma Spray</td>
<td>Plasma Spray</td>
<td>Arc Ion Plating</td>
<td>Arc Ion Plating</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>fcc</td>
<td>Tetragonal</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>a₀=7.60</td>
<td>a₀=5.10, c₀=5.19</td>
<td>a₀=4.58</td>
<td>a₀=4.52</td>
</tr>
<tr>
<td>Characteristic X-ray</td>
<td>Co-Kα</td>
<td>Cr-Kα</td>
<td>Co-Kα</td>
<td>Co-Kα</td>
</tr>
<tr>
<td>Diffraction plane</td>
<td>(310), 2θ=128.66°</td>
<td>(133), 2θ=152.35°</td>
<td>(422), 2θ=148.50°</td>
<td>(422), 2θ=151.40°</td>
</tr>
<tr>
<td>Tube voltage (kV)</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tube current (mA)</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detector</td>
<td>Scintillation counter</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irradiated area (m²)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed time (sec)</td>
<td>16.8</td>
<td>13.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Step width (deg)</td>
<td>0.27</td>
<td>0.12</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Incident beam angle (deg)</td>
<td>-24, -14.1, 21</td>
<td>0.15, 30.45</td>
<td>0.15, 30.45</td>
<td>-24, -14, -4.6</td>
</tr>
<tr>
<td>Facility</td>
<td>△</td>
<td>△</td>
<td></td>
<td>△</td>
</tr>
</tbody>
</table>

### Table 3 Mechanical and X-ray elastic constants.

<table>
<thead>
<tr>
<th>Material</th>
<th>TiC (CVD)</th>
<th>TiC (CVD)</th>
<th>TiN (CVD)</th>
<th>TiN (CVD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Later heat treatment</td>
<td>Quenched &amp; tempered</td>
<td></td>
<td>Quenched &amp; tempered</td>
<td></td>
</tr>
<tr>
<td>E₀ (GPa)</td>
<td>42.1</td>
<td>4.89</td>
<td>4.52</td>
<td>5.65</td>
</tr>
<tr>
<td>Diffraction plane</td>
<td>(115)</td>
<td>(113)</td>
<td>(420)</td>
<td>(420)</td>
</tr>
<tr>
<td>(112)/E₀ (1/GPa)</td>
<td>2.39×10⁻³</td>
<td>1.13×10⁻³</td>
<td>2.15×10⁻²</td>
<td>1.81×10⁻²</td>
</tr>
<tr>
<td>ν/E₀ (1/GPa)</td>
<td>3.97×10⁻¹</td>
<td></td>
<td>2.55×10⁻²</td>
<td>4.42×10⁻²</td>
</tr>
<tr>
<td>E₁ (GPa)</td>
<td>3.97</td>
<td></td>
<td>5.24</td>
<td>7.30</td>
</tr>
<tr>
<td>ν₁</td>
<td>0.16</td>
<td></td>
<td>0.13</td>
<td>0.33</td>
</tr>
<tr>
<td>K (GPa/deg)</td>
<td>-1.67</td>
<td>-4.30</td>
<td>-7.41</td>
<td>-1.68</td>
</tr>
<tr>
<td>σ (GPa)</td>
<td>-2.48</td>
<td>-3.52</td>
<td>-3.42</td>
<td>2.53</td>
</tr>
<tr>
<td>Material</td>
<td>TiB₂</td>
<td>Al₂O₃ (0.2nm)</td>
<td>Al₂O₃ (0.3nm)</td>
<td>Al₂O₃ (0.5nm)</td>
</tr>
<tr>
<td>E₀ (GPa)</td>
<td>407</td>
<td>6.3</td>
<td>3.5</td>
<td>7.7</td>
</tr>
<tr>
<td>Diffraction plane</td>
<td>(222)</td>
<td>(800)</td>
<td>(800)</td>
<td>(800)</td>
</tr>
<tr>
<td>(112)/E₀ (1/GPa)</td>
<td>1.89×10⁻³</td>
<td>4.55×10⁻³</td>
<td>8.35×10⁻²</td>
<td>3.28×10⁻²</td>
</tr>
<tr>
<td>ν/E₀ (1/GPa)</td>
<td>2.45×10⁻³</td>
<td>4.76×10⁻²</td>
<td>16.43×10⁻²</td>
<td>4.10×10⁻²</td>
</tr>
<tr>
<td>E₁ (GPa)</td>
<td>6.09</td>
<td>2.40</td>
<td>1.49</td>
<td>3.50</td>
</tr>
<tr>
<td>ν₁</td>
<td>0.15</td>
<td>0.11</td>
<td>0.24</td>
<td>0.14</td>
</tr>
<tr>
<td>K (GPa/deg)</td>
<td>-1.61</td>
<td>-0.80</td>
<td>0.19</td>
<td>-1.25</td>
</tr>
<tr>
<td>σ (GPa)</td>
<td>-1.38</td>
<td>+0.83</td>
<td>+0.30</td>
<td>+1.08</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Elastic Constants

Table 3 shows the mechanical and X-ray elastic constants. For example, mechanical elastic constants of as-coated TiN and quenched-tempered one were 452(GPa) and 565(GPa), respectively. 26-sin²ψ diagrams of X-ray method can be approximated by straight lines in all ceramic coated films. Figure 1 shows the linear relation between the slope(M) and the applied stress(σ_M) in TiN(420) plane. Figure 2 shows the relation between 2θ and σ_M. From Eqs.(1) and (2), the compliances S₂/2, S₁ and the stress constant(K) can be determined experimentally. Table 3 shows also the X-ray elastic constants and stress constants. The X-ray elastic constant of as-coated was 524(GPa) for TiN(420) plane and quenched-tempered was 730(GPa), those were higher than the mechanically determined values.

Residual Stress Distribution

Figure 3 shows the residual stress distribution in TiN coated steels. It indicated high compressive stress above -3.5(GPa) in the as-coated TiN film. Compressive stress was existed within TiN film and tensile stress was existed within substrate. It is caused by the thermal expansion mismatch.

Fig. 1. Relation between slope of 2θ-sin²ψ diagram(M) and applied stress(σ_M) in TiN(420) plane.

Fig. 2. Relation between intercept of 2θ-sin²ψ diagram(2θ_0) and applied stress(σ_M) in TiN(420) plane.
Plane Bending Fatigue Test

Figure 4 shows the S-N curves of plane bending fatigue test. Quenched-tempered TiN coated steels indicated the highest fatigue strength. Fatigue limit was 292 (MPa), that was increased about 100 (MPa) compared with as-coated.

Figure 5 shows the changes in residual stress of TiN layer and substrate during high stress amplitude fatigue process. Surface compressive residual stress in TiN film and tensile residual stress in substrate were decreased gradually with the fatigue progress. It was corresponded to the stress release of crack propagation. It was expected to detect the fatigue damage accumulation.

Sliding Wear Test

Figure 6 shows the relation between variation of wear loss and sliding distance. TiN coated steels had higher wear resistance than non-coated steels. And quenched-tempered later heat treated steels were better than as-coated one.

Figure 7 shows the relation between residual stress of substrate and sliding distance. As the wear distance became more, residual stress increased to compressive side. The residual stress increased corresponding to the extend of plastic flow area. The X-ray method was applied effectively as a nondestructive detecting method of sliding wear damage accumulation.
Fig. 4. S-N curves of plane bending fatigue.

Fig. 5. Changes of residual stress values during plane bending fatigue. ($\sigma_a=429\text{MPa}$, $N_f=2.1\times10^4$)
Fig. 6. Relation between variation of wear loss and sliding distance.

Fig. 7. Relation between residual stress of substrate and sliding distance in quenched-tempered later heat treated TiN coated steels. (Load=245N)
CONCLUSION

The X-ray method was successfully applied to measure the residual stress distribution and residual stress changes during fatigue and wear processes in ceramics coated steels.

Neutron diffraction has been used to measure the residual stress distributions in steels. Bourke et. al reported in uncracked and fatigue cracked rings taken from a high strength, low alloy steel autofrettaged tube with a bore diameter of 60(mm) and a wall thickness of 32(mm).(8) Figure 8 shows the hoop residual stresses in the uncracked sides of the 14%, 25% and 50% fatigue cracked rings. Neutron residual stress measurement is effective to ceramic thin films, because the wave length is long and petration depth is shallow.
REFERENCES


APPLICATION OF NEUTRON SPIN ECHO SPECTROSCOPY TO DYNAMICAL BEHAVIORS OF CONDENSED MATTER

Shigehiro KOMURA, Takayoshi TAKEDA and Hideki SETO
Faculty of Integrated Arts and Sciences, Hiroshima University
1-7-1, Kagami-yama, Higashi-Hiroshima-shi, 724 Japan

ABSTRACT

Some applications of neutron spin echo spectroscopy to dynamical behaviors of several systems are discussed and envisaged for the newly built neutron spin echo spectrometer at JRR-3M. In particular the dynamics of shape fluctuation in "water-in-oil" microemulsion droplet system is discussed in some detail. It is shown that the relaxation time of the over-damped motion of the shape fluctuation to restore the spherical form may depend on the spontaneous radius of the surfactants. It is stressed that a plenty of systems whose dynamical behaviors have ever been studied so far by neutron scattering await the present day renovation of data by means of neutron spin echo spectrometer that allows highest resolution of transferred wavevector and frequency ever achieved using neutrons.

INTRODUCTION

Neutron spin echo spectroscopy is a well established inelastic scattering method that allows the highest resolution of transfer energy of all neutron spectroscopies. A combination of small angle neutron spectrometer with the spin echo spectroscopy makes it possible to study mesoscopic spatial structure of the order of $1\sim10^2$ nm combined with nanosecond temporal structure of the order of $10^1\sim10^3$ ns, the spatio-temporal region much larger than that of atomic motions, but smaller than our daily experiences.

We have designed and have been constructing a neutron spin echo spectrometer at the beam port C2-2 of JRR-3M reactor, JAERI, Tokai, using a cosine-shaped optimal magnetic field for neutron spin precession as proposed by Zeyen. The details of the spectrometer are described elsewhere. The spectrometer will be commissioned within the 1993 fiscal year. The areas of study using the spin echo spectrometer are classified into the following three categories.

I. Dynamical behaviors of large assemblies made of medium sized molecules. In complex fluids, such as liquid crystal, surfactant/water/oil system and lipid/water system, small molecules make up large assemblies, like smectic layers, micells, vesicles, lamella, microemulsions and so on. The collective motions of these objects are candidates to be studied by neutron spin echo method.

II. Dynamical behavior of assemblies of large molecules. In polymer or biological systems, the chain lengths extend sometimes to $10^4\sim10^6$ molecular weights or the molecular sizes amount to several hundred nm. The collective motions of such objects are another kinds of candidates.
III. Dynamical critical behavior of condensed matter.
As formulated by Halperin and Hohenberg 2) in the late 1960's, the dynamical scaling law at the
critical region of condensed matter made of atoms or small molecules are one of the most
challenging problems to be tested by present sophisticated neutron spectroscopy. In comparison
with the static scaling law that is believed to be well established, there are still many points of
dynamical behaviors that await the probing by neutron spin echo spectroscopy.

In this report some interesting topics from the I and III of the above categories are
illustrated and discussed in some details to demonstrate the feasibilities of the spectrometer.

DYNAMICS OF DIFFUSIVE MOTION

The dynamical behavior of any fluctuating system is described by a correlation functions
$S^{AB}(q, \omega)$ as functions of the scattering vector $\vec{q}$ and the transferred frequency $\omega$,
which is a Fourier transform of space-time correlation function $\langle \phi^A(\vec{r}, t) \phi^B(0, 0) \rangle$
of the order parameter $\phi^A(\vec{r}, t)$ and $\phi^B(\vec{r}, t)$ as functions of space $\vec{r}$ and time $t$. It is to be stressed that the neutron spin
echo spectrometer offers a direct measurement of the intermediate correlation function $I^{AB}(\vec{q}, t)$.
Therefore in case of both classical monoatomic fluids and hydrodynamical limit of spin
diffusion in magnetic systems we have

$$ I(\vec{q}, t) = \exp(-\Gamma(\vec{q}) t) \ I(\vec{q}, 0) \tag{1} $$

which corresponds to

$$ S(\vec{q}, \omega) = \frac{1}{\pi h} \ \frac{\Gamma(\vec{q})}{\omega^2 + \Gamma(\vec{q})^2} \ I(\vec{q}, 0) \tag{2} $$

where $\Gamma(\vec{q}) = D_{eff} q^2$ represents the energy width due to the diffusional motion of the order
parameter with an effective diffusion constant $D_{eff}$. It is customary to obtain the energy width
$\Gamma(\vec{q})$ by calculating

$$ \Gamma(\vec{q}) = \lim_{t \to 0} -\frac{1}{I(\vec{q}, 0)} \ \frac{\partial I(\vec{q}, t)}{\partial t} \tag{3} $$

from the measured $I(\vec{q}, t)$. The effective diffusion constant is further calculated by

$$ D_{eff} = \frac{\Gamma(\vec{q})}{q^2} $$

APPLICATION TO THE DYNAMICS OF SPHERICAL DROPLETS

Perhaps the most interesting example of applications of the neutron spin echo
spectroscopy belonging to the category of I (Dynamical behavior of large assemblies made of
medium-sized molecules) is that of microemulsions consisting of spherical droplets. In a "water-in-oil" microemulsion system water droplets are coated with surfactant films and dispersed in
solvent consisting of oil. The droplet size is typically 10 nm. The spherical form of the droplet
may deform by thermal fluctuation but restore the spherical form by over-damped motion driven
by bending elasticity of the film membrane (Fig.1).

The dynamical fluctuation of droplet microemulsions of this kind is investigated
theoretically by the pioneering work of Milner and Safran 3) and tested experimentally by Huang
et al. using neutron spin echo spectrometry. It was clarified by the experiment that the over-damped motion of the shape fluctuation is driven not by surface tension but by elastic bending forces. From the analysis of the experiment along the theory of Milner and Safran, the value for the bending elasticity $K_c$ was estimated to be $K_c = 5 k_B T$, which seems eminently reasonable in view of the premature stage of the theory in this field.

Komura, Jr. and Seki\(^5\) have recently reformulated the equilibrium shape of spherical droplets on the basis of minimization of the following shape energy of the membrane

$$
H = \frac{1}{2} K_c \int dA \left( r_1^{-1} + r_2^{-1} + r_3^{-1} \right)^2 + \sigma \int dA + \Delta p \int dV
$$

(4)

where $dA$ and $dV$ are surface and volume elements of droplets, respectively, $r_1$ and $r_2$ are two principal radii of curvature, $r_3$ the spontaneous radius of curvature, $\sigma$ the surface tension and $\Delta p = p - p'$ the difference of the osmotic pressures $p$ and $p'$ between outside and inside a droplet, respectively. They have then derived the formula of the relaxation times of the over-damped modes without "constant excess area" which was introduced by Milner and Safran in somewhat artificial way in addition to the constraints of constant surface and constant volume of the droplets.

The deformation of a droplet from a sphere can be expressed by a translational (out of plane) displacement $a(\theta, \phi, t)$, that depends on the position on the sphere defined by the polar angle $\theta$ and $\phi$ and on time $t$, which is in turn expanded in terms of the spherical harmonics $Y_{nn}(\theta, \phi)$ as

$$
a(\theta, \phi, t) = \sum_{n,m} a_{nm}(t) Y_{nm}(\theta, \phi)
$$

(5)

The equation of motion of the coefficients of the translational displacements is given by

$$
\ddot{a}_{nm}(t) = -\gamma_n \dot{a}_{nm}(t) - \omega_n^2 a_{nm}(t)
$$

(6)

Fig.1 Shape fluctuation of "water-in-oil" microemulsion droplet. A sphere with a radius $r_0$ is deformed by the translational displacement $a(\theta, \phi, t)$. 

--- 955 ---
in terms of the frictional constant $\gamma_n$ and the oscillation frequency $\omega_n$. In case of large damping force the term $a_{mn}(t)$ can be neglected and $a_{mn}(t)$ is approximated by

$$a_{mn}(t) = a_{mn}(0) \exp(-\lambda_n t)$$  \hspace{2cm} (7)

with the damping constant $\lambda_n$ defined as the inverse of the relaxation time $\tau_n$.

$$\lambda_n = \tau_n^{-1} = \frac{\omega_n^2}{\gamma_n}$$  \hspace{2cm} (8)

The formula for the damping frequency of the $n$-th mode $\lambda_n$ by Milner and Safran is given by

$$\lambda_n = \frac{K_c}{\eta_0^3} \frac{n(n+1)(n+2)(n-1)(n+3)(n-2)+4w}{2n+1(2n^2+2n-1)}$$  \hspace{2cm} (9)

where $\eta$ is the viscosity of the solvent, $r_0$ the droplet radius, $w = r_0/r_s$, neglecting the entropy term. This formula is compared to the equivalent one by Komura, Jr. and Seki as given by

$$\lambda_n = \frac{K_c}{\eta_0^3} \frac{(n-1)n(n+1)(n+2)(2n+1)(E+1)E+2n(n+2)}{2(n^2-1)E+2n^2+1}[n(n+1)-2w+\frac{1}{2}w^2]$$  \hspace{2cm} (10)

where $E = \eta'/\eta$ with $\eta'$ the viscosity inside the droplet.

Since $n=1$ gives a translational diffusive motion of droplets, we have the lowest mode of shape deformation for $n=2$. Putting $w=1$ ($r_0=r_s$) and $E=1$ ($\eta' = \eta$) for simplicity, we get $\lambda_2 = \frac{K_c}{\eta_0^3} \frac{96}{55}$ from (9) and $\lambda_2 = \frac{K_c}{\eta_0^3} \frac{72}{35}$ from (10). The both resules give the same value of $\lambda_2 = 4 \times 10^7$ s$^{-1}$ if we use the values $K_c \sim 2 \times 10^{-20}$ J$\sim 5k_BT$, $\eta \sim 10^{-3}$ Kg/m.s, $r_0 \sim 10^{-3}$ m. However putting $w=0.5$ ($r_s = 2r_0$), they give quite different values $\lambda_2 = \frac{K_c}{\eta_0^3} \frac{48}{55}$ from (9) and $\lambda_2 = \frac{K_c}{\eta_0^3} \frac{82}{35}$ from (10) by a factor more than 2. Such dependence of $\lambda_n$ on the value of $r_s$ is one of the points that await the probing by precise measurement of neutron spin echo spectroscopy.

In a real experiment the intermediate correlation function can be written according to Milner and Safran$^3$ as

$$I(q,t) = \frac{N_p V_p^2}{V_s} (\Delta \rho)^2 \exp(-Dq^2t) \left[ f_0(qr_0) + \sum_{n=1}^{2n+1} \frac{2n+1}{4\pi r_0^3} f_n(qr_0) \langle a_n(t) a_n(0) \rangle \right]$$  \hspace{2cm} (11)

where $V_s$ is the sample volume, $N_p$ the droplet density per unit volume of the sample, $V_p$ the volume of a droplet particle, $\Delta \rho$ the difference of the scattering amplitude density between the droplet and the solvent; Here the static form factor of the droplet is $f_0(z) = [j_0(z)]^2$ for the shell and $f_0(z) = [3j_1(z)/z]^2$ for the sphere; the inelastic form factor is $f_n(z) = [(n+2)j_{n}(z) - 2j_{n-1}(z)]^2$ for the shell and $f_n(z) = [3j_n(z)]^2$; $j_0(z)$ and $j_n(z)$ being the spherical Bessel functions.
Therefore according to the formula (3), the effective diffusion coefficient is given by

\[
D_{\text{eff}} = \frac{\Gamma(q)}{q^2} = D + \frac{3\lambda_2 f_2(qr_0)}{q^2[4\pi^2 f_0(qr_0) + 3f_2(qr_0) \{ |\alpha_2|^2 \}]}
\]  

(12)

up to the lowest mode \( n=2 \) \((\alpha_2 = \alpha_2(0))\).

Such behavior as the formula (12) was really observed by Huang et al.\(^4\). The effective diffusion coefficient \( D_{\text{eff}}(q) \) as a function of \( q \) reveals, above a constant value \( D \), a maximum at the value \( q=q_m \) for which \( f_0(qr_0) \) becomes zero or \( q_m r_0 = \pi \) (Fig.2).

The value of \( D \), for which the Stokes Formula

\[
D = \frac{k_B T}{6\pi \eta r_0}
\]

(13)

was assigned implicitly in the analysis of Huang et al, should be checked if the formula

\[
D = \frac{k_B T}{2\pi \eta r_0 \left( 2\eta + 3\eta' \right)}
\]

(14)

is applied as proposed by Komura Jr. and Seki for \( n=1 \) mode that gives translational diffusive mode. The formula (14) reduced to (13) in the case of \( \eta' \rightarrow \infty \) corresponding to a solid sphere. For \( E=1 \ (\eta' = \eta) \) (14) becomes

\[
D = \frac{k_B T}{5\pi \eta r_0}
\]

(15)

The dependence of \( D \) on \( E=\eta'/\eta \) in the formula (12) is another point of interest to be tested by the neutron spin echo spectroscopy.

Fig. 2 Effective diffusion coefficient \( D_{\text{eff}} \) as calculated from the intermediate correlation function \( I(\vec{Q},t) \) by the formula (3) (schematic). It has a peak at \( q_m \) \((q_m r_0 = \pi)\) for which small angle scattering intensity \( I(q) \) has a minimum.
APPLICATION TO THE DYNAMICAL CRITICAL BEHAVIOR

Among the category III (Dynamical behavior of condensed matter) there is a plenty of systems that await the present day renovation of critical data by means of neutron spin echo spectroscopy that allows the highest resolution of transferred wavevector and frequency ever achieved using neutrons. The improvements of critical indices data are particularly required in view of the successful application of the renormalization group theory as developed by C.G. Wilson in the 1970's to calculate the reliable critical indices of various universality classes.

It is also very interesting to investigate the dynamical critical behaviors of the "water-in-oil" droplet system that we have discussed in the last chapter. The system undergoes the phase separation at elevated temperature above the room temperature in a way that the droplet density in one phase is higher than in another, while the droplet size remains almost the same in both phases. Seto et al.\(^5\) have studied the static critical phenomena in this system and found that the system behaves with the critical indices of the mean-field values within certain temperature range below the critical point in contrast to those of 3D Ising values that have been observed in other researchers. This point should be further clarified through the dynamical critical study by means of neutron spin echo spectroscopy.

Another interesting subject is the spin fluctuation in an Fe\(_{55}\)Ni\(_{35}\) invar alloy near its critical point. According to our earlier study\(^7\) by neutron spin echo spectroscopy the alloy is magnetically inhomogeneous and exhibits poly-dispersive spin diffusion coefficients \(D_i\) such that the intermediate correlation function is expressed as

\[
I(q,t) = \sum_{i=1}^{n} p(D_i) \exp(-D_i q^2 t) I(q,0)
\]  

(16)

where \(p(D_i)\) is the weighting functions with \(\sum_{i=1}^{n} p(D_i) = 1\). \(n\) being at least more than 2. Such an unusual critical behavior in inhomogeneous system should further be tested.

REFERENCES

NEUTRON SPIN ECHO SPECTROMETER AT JRR-3M

Takayoshi TAKEDA, Shigehiro KOMURA, Hideki SETO, Michihiro NAGAI, Hideki KOBAYASHI, Eiji YOKOI, T ooru EBISAWA and Seiji TASAKI

Faculty of Integrated Arts and Sciences, Hiroshima University
1-7-1 Kagamiyama, Higashi-hiroshima-shi, 724 Japan

*Research Reactor Institute, Kyoto University
Noda, Kumatori-cho, Sen-nan-gun, Osaka-fu, 590-04 Japan

ABSTRACT

We have designed and have been constructing at C2 cold neutron guide port of JRR-3M, JAERI, a neutron spin echo spectrometer (NSE) which is equipped with two optimized magnets for neutron spin precession, a position sensitive detector (PSD), a converging polarizer and a wide area analyzer. The dynamic range of scattering vector Q covers from 0.01 Å⁻¹ to 0.3 Å⁻¹ and that of energy E from 30 meV to 0.1 meV. This spectrometer makes it possible to study a mesoscopic spatial structure of the order of 1-100 nm combined with a nanosecond temporal structure of the order of 0.1-100 ns corresponding to dynamical behavior of large molecules such as polymer. A test experiment shows that the homogeneity condition of the precession magnet is loosened by means of PSD.

INTRODUCTION

The neutron spin echo (NSE) method proposed by Mezei provides an extremely high energy resolution in analyzing small energy changes on scattering as a phase shift in the Larmor precession of each neutron spin in a magnetic field.¹ The wave vector Q and Fourier time t dependent correlation function I(Q,t) of an investigated system is observed directly in the NSE experiment. Then S(Q,γ) can be calculated from I(Q,t) by means of Fourier transformation. The Fourier time t is given as

\[ t = (2\pi|\mu|nm^2/h^3)\lambda^3 D \]

or in unit of s,

\[ t[s] = 1.8635 \times 10^{-10} \lambda^3 [\text{Å}] D [\text{Tm}] , \]  

where \( \lambda \) is the neutron wavelength in unit of Å and \( D \) the magnetic field integral in unit of Tm. The magnetic field integral \( D \) along the neutron path is given by,

\[ D = \int |B| dl = \int \left( B_x^2 + B_y^2 + B_z^2 \right)^{1/2} dl , \]
where $B_z$, $B_r$, and $B_\phi$ are the axial $z$, radial $r$ and azimuthal $\phi$ components of the magnetic field $B$. df is the element of the length along the neutron path. The dynamic range of $r$ can be varied by the magnetic field strength. The maximum Fourier time $t_m$ or maximum field integral $D_m$ determines the achievable spectral resolution $\Delta E = \hbar \Delta \omega$ of the spectroscopy. The spectral resolution $\Delta E$ is defined by,

$$\Delta E = \hbar \Delta \omega = 0.05 \hbar t_m .$$

(3)

On the other hand, the energy resolution $\delta E$, which is determined by the inhomogeneity of $D$, in contrast to $\Delta E$ is given by,

$$\delta E = 2 \frac{\Delta D}{D} E .$$

(4)

where $\Delta D$ is inhomogeneity of $D$ and $E$ is the energy of the incident neutrons.

We have designed an NSE spectrometer in order to study a mesoscopic spatial structure of the order of 1~100nm combined with a nanosecond temporal structure of the order of 0.1~100ns corresponding to dynamical behavior of large assemblies made of medium-sized molecules and assemblies of large molecules and also to dynamical critical behavior of condensed matters. The NSE spectrometer shares the C2-2 cold guide port of JRR-3M, the monochromator, the neutron guide, the sample table and the dancing floor commonly with the neutron spectral modulation spectrometer(NSM). The parts which are shared with the NSM spectrometer and the tables for the polarizer, precession coil, analyzer and detector have been constructed. Other parts are being constructed. The precession coil will be constructed by the end of March 1993.

We have carried out a test experiment of NSE using the parts constructed and the parts of another NSE spectrometer which we had constructed at KUR.

In this paper, we give the design of the NSE spectrometer and that of the precession coil in detail. Finally, we demonstrate in the test experiment of NSE that the homogeneity condition of the precession magnet is loosened by means of the position sensitive detector(PSD).

**Fig. 1** The whole view of the neutron spin echo spectrometer at JRR-3M. C2-2 : C2-2 cold neutron guide port, M : monochromator, G : neutron guide, P : polarizer, PF : precession coil, S : sample, A : analyzer and D : detector

**DESIGN OF THE SPECTROMETER**
We have designed an NSE spectrometer at the C$_{23}$ cold neutron guide port of JRR-3M as shown in Fig. 1. The dynamic range of scattering vector $Q$ covers from 0.01Å$^{-1}$ to 0.3Å$^{-1}$ and that of energy $E$ from 30neV to 0.1meV. Some of the design parameters of the spectrometer are listed in Table 1. The reflected neutrons by a multi-layer monochromater at the C$_{23}$ port pass through a 9m neutron guide and reach a polarizer. The monochromater has a wavelength resolution of about 10% in the wavelength range 5–8Å. The distance between the monochromater and polarizer is about 12m. The polarizer, the precession coil, the analyzer and the detector table move freely on the dancing floor and the reflecting and scattering angles at the monochromater, the polarizer, the sample and the analyzer are set by a computer control. These tables have been constructed. The distance between the polarizer and the sample table is about 3.5m, that between the sample table and the analyzer 3.5–3.9m, and that between the analyzer and the detector 3–3.5m. Fig. 2 shows the set up of the NSE spectrometer in detail. It consists of the following parts: A: polarizer, B: magnetic guide, C:

| Table 1 |
| Design parameters of the neutron spin echo spectrometer |

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic range $Q$</td>
<td>0.01 Å$^{-1}$ – 0.3 Å$^{-1}$</td>
</tr>
<tr>
<td>$E$</td>
<td>30 neV – 100 μeV</td>
</tr>
<tr>
<td>Path length in precession field $L$</td>
<td>2.6 m</td>
</tr>
<tr>
<td>Maximum field integral</td>
<td>0.22 Tm</td>
</tr>
<tr>
<td>Relative inhomogeneity of field integral</td>
<td>$\eta = \Delta D/D &lt; 2 \times 10^{-6}$</td>
</tr>
<tr>
<td>Maximum spin turn number $N$</td>
<td>$\lambda = 5 \text{ Å}$</td>
</tr>
<tr>
<td>Maximum Fourier time $t$ (ns)</td>
<td>8109</td>
</tr>
<tr>
<td>Spectral resolution $\Delta E$ (neV)</td>
<td>5.0</td>
</tr>
<tr>
<td>Energy resolution $\delta E$ (neV)</td>
<td>6.4</td>
</tr>
<tr>
<td>Wavelength</td>
<td>$\lambda = 8 \text{ Å}$</td>
</tr>
<tr>
<td>Wavelength resolution $\Delta \lambda/\lambda$</td>
<td>13.1</td>
</tr>
<tr>
<td>5 – 8 Å</td>
<td>5.1</td>
</tr>
<tr>
<td>Beam cross section at monochromater</td>
<td>10%</td>
</tr>
<tr>
<td>Polarizer</td>
<td>$20^w \times 50^h \text{ mm}$</td>
</tr>
<tr>
<td>Sample</td>
<td>$20^w \times 50^h \text{ mm}$</td>
</tr>
<tr>
<td>4th $\pi/2$ coil</td>
<td>$20^p \text{ mm}$</td>
</tr>
<tr>
<td>Analyzer</td>
<td>$120^p \text{ mm}$</td>
</tr>
<tr>
<td>Detector</td>
<td>$60^w \times 150^h \text{ mm}$</td>
</tr>
<tr>
<td>Distance between</td>
<td>$12^w \times 300^h \text{ mm}$</td>
</tr>
<tr>
<td>Monochromater-polarizer</td>
<td>~ 12m</td>
</tr>
<tr>
<td>Polarizer-sample</td>
<td>~ 3.5m</td>
</tr>
<tr>
<td>Sample-analyzer</td>
<td>3.4 – 3.9m</td>
</tr>
<tr>
<td>Analyzer-detector</td>
<td>3.0 – 3.5m</td>
</tr>
</tbody>
</table>
Fig. 2  The set-up of the neutron spin echo spectrometer at JRR-3M

A : polarizer  
A-1 : polarizer  
A-2 : magnet  
A-3 : polarizer table  
B : magnetic guide (vacuum tube)  
C : 1st $\pi/2$ coil  
C-1 : $\pi/2$ coil  
C-2 : correction coil  
D : 1st precession coil  
D-1 : precession coil  
D-2 : spiral coils  
D-3 : vacuum tubes  
E : 2nd $\pi/2$ coil or $\pi$ coil  
E-1 : $\pi/2$ coil or $\pi$ coil  
E-2 : correction coil  
F : 1st precession coil table  
G : sample table  
G-1 : goniometer  
G-2 : stage  
G-3 : coils (x-y-z)  
G-4 : sample  
H : 2nd precession coil table  
I : 3rd $\pi/2$ coil  
I-1 : $\pi/2$ coil  
I-2 : correction coil  
J : 2nd precession coil  
J-1 : precession coil  
J-2 : spiral coils  
J-3 : vacuum coil  
J-4 : symmetry coil  
K : 4th $\pi/2$ coil  
K-1 : $\pi/2$ coil  
K-2 : correction coil  
L : magnetic guide (vacuum tube)  
M : analyzer  
M-1 : analyzer  
M-2 : magnet  
M-3 : goniometer  
N : detector  
N-1 : position sensitive detectors  
N-2 : vacuum tube  
O : slits  
P : beam stoppers  
Q : monitor detector  
R : beam shutter
\( \pi/2 \) and correction coil, D: precession coil with spiral correction coils, E: \( \pi/2 \) (or \( \pi \)) and correction coil, F: precession coil table, G: sample table with correction coils, H: precession coil table, I: \( \pi/2 \) and correction coil, J: precession coil with spiral correction coils, K: \( \pi/2 \) coil and correction coil, L: magnetic guide, M: analyzer, N: detector, O: slits, P: beam stoppers. The polarizer (or the analyzer) is a Soller slit type assembly of magnetic supermirrors which are composed of sheets of silicon wafers with alternating layers of Co-Fe alloy and V metal on them. The cross section of the incident beam at the polarizer is \( 20^\circ \times 50^\circ \text{mm}^2 \). The reflected neutrons by the polarizer converge at the analyzer position in order to improve the \( Q \) resolution without sacrificing the intensity. Diverging scattered neutrons from the sample are reflected by the analyzer with a beam cross section of \( 60^\circ \times 150^\circ \text{mm}^2 \) and detected by the position sensitive detector which specifies different divergent neutron paths. The detector is an assembly of 15 1D-PSDs of \( 1/2 \) inch in diameter. Each 1D-PSD is set vertically. The long distance between the analyzer and the detector reduces the neutron noise without sacrificing available intensity using PSDs.

**PRECESSION COIL**

For the magnet that facilitates the Larmor precession of neutron spins, we have adopted the optimal field shape coil (OFS coil) as proposed by Zeyen, which has a sinusoidal field distribution \( B_z(z) \) along the axial coordinate \( z \) (approximately parallel to the neutron path) over a length \( L \) such that,

\[
B_z(z) = B_0 \cos^2 \left( \frac{\pi z}{L} \right).
\]  

(5)

For a long conventional simple solenoid, the relative field-integral inhomogeneity \( \eta \) is given as,

\[
\eta = \frac{\Delta D}{D} - \frac{r^2}{2D_L L_s}.
\]

(6)

where \( D_s \) is the solenoid diameter, \( L_s \) the length of the solenoid and \( r \) the radial coordinate of the neutron trajectory. For the OFS coil, the relative field integral inhomogeneity \( \eta \) is given as,

\[
\eta = \frac{1}{2} \left( \frac{D_L}{L_s} \right)^2.
\]

(7)

The spin flippers such as \( \pi/2 \) coil and \( \pi \) coil are operated at \( z = \pm L/2 \) positions with on origin \( z = 0 \) defined at the center of the coil. Since \( \eta \)

<table>
<thead>
<tr>
<th>Table 2. Design parameters of the precession coil.</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnetic length ( L )</td>
</tr>
<tr>
<td>number of subcoils</td>
</tr>
<tr>
<td>bore of 1st subcoil</td>
</tr>
<tr>
<td>maximum field integral</td>
</tr>
<tr>
<td>inhomogeneity without correction</td>
</tr>
<tr>
<td>inhomogeneity with 2 spiral coils</td>
</tr>
<tr>
<td>maximum current</td>
</tr>
<tr>
<td>maximum field</td>
</tr>
<tr>
<td>number of windings</td>
</tr>
<tr>
<td>hollow conductor wire</td>
</tr>
<tr>
<td>electrical resistance</td>
</tr>
<tr>
<td>cooling system</td>
</tr>
<tr>
<td>capacity of the refrigerator</td>
</tr>
</tbody>
</table>
does not couple with $D$, directly, we can reduce the coil diameter in the OFS coil. Decreasing the diameter of the coil reduces not only the stray field but the cost of the precession coil. The inhomogeneity $\eta$ proportional to $r^2$ in eq. (7) is corrected by means of a Mezei's Fresnel spiral coil. Even for a divergent neutron path, the inhomogeneity $\eta$ is corrected well by two spiral coils positioned at $z=\pm 0.366L$ in the case of the OFS coil.

The OFS coil of this spectrometer consists of 20 coaxial subcoils having different length and diameters stacked together. The bore of the first and the 20th subcoil is 219mm and 503mm, respectively, and the length of the first and the 20th subcoil is 2080mm and 273mm, respectively. Some of the design parameters of the coil are listed in Table 2. The maximum field integral $D_{\text{m}}$ of the coil is 0.22 Tm. The magnetic length $L$ is 2.6m. The field distribution $B_d(z,r)$ and $B_d(z,r)$ at $r=2\text{cm}$ calculated from the OFS coil without any correction coils is shown in Fig. 3. In the curve of $B_d(z,r)$, wiggles appear at the ends of the subcoils and they increase with increasing $r$. Though the wiggles cause the neutron depolarization, the depolarization is negligible in this OFS coil for $r<4\text{cm}$ which was designed in the following condition:

$$\left[ \frac{\sin^{-1}(B_r(z, r, \phi)/B_d(z, r, \phi))}{dz} \right]/B(z, r, \phi) < 1000 \text{T}^{-1} \text{m}^{-1},$$

where the speed of the spin rotation in the Lamor precession is at least 200 times more than that of the magnetic field direction for a moving neutron spin.

The deviation of the field integral $D$ from the axial symmetry (the $\phi$ dependence of $D$) caused from wide conductor wires, typically 12mm wide and 6mm high, was a serious problem. The inhomogeneity from the deviation cannot be corrected by the spiral coil. The winding of the conductor wires and the interconnection between the subcoils were designed in such a way as to compensate the deviation as far as possible. Fig. 4 shows the $\phi$ dependence of the inhomogeneity $\Delta D_r(r, \phi)$ of $D$ in the OFS coil caused from wide conductors; $\Delta D_r(r, \phi)$ is given by,
\[ \Delta D_1(r, \phi) = \int_0^{L/2} [B(z, r, \phi) - B^0(z, r)] \, dl, \]  

(9)

where \( B(z, r, \phi) = (B^2(z, r, \phi) + B^2(z, r, \phi) + B^2(z, r, \phi))^{1/2} \) and \( B^0(z, r) \) is the magnetic field calculated from a coil with the axial symmetry. The \( \phi \) dependence of \( \Delta D/D \) is less than \( 1.5 \times 10^{-6} \) for \( r=3 \text{cm} \). \( \Delta D_1(r, \phi) \) compensates itself much more when the integration range covers from \(-L/2\) to \(L/2\). The total relative inhomogeneity \( \eta \) of the spectrometer for \( 44 \text{cm} \) neutron beam is to be reduced below \( 2 \times 10^{-6} \) by means of the spiral coils.

**Fig. 4** The \( \phi \) dependence of the relative inhomogeneity of the field integral \( D \) in the OFS precession coil caused from wide conductor wires.

**Fig. 5** The setup of the test experiment of NSE in order to show the advantage of PSD for the homogeneity condition.

**ADVANTAGE OF USING THE POSITION SENSITIVE DETECTOR FOR THE HOMOGENEITY CONDITION**

We have carried out a test experiment of NSE in order to show the advantage of using the PSD for the homogeneity condition. The setup of the NSE experiment is shown in Fig. 5. P: polarizer, \( \pi/2: \pi/2 \) coil, PF: precession coil, Al-Zn-Mg: sample, A: analyzer. The field
integral $D$ was 0.015Tm and $\lambda$ =7A. We observed the NSE signal of neutrons scattered elastically from ternary Al alloy with 10% Zn and 0.1% Mg aged at 80 °C. The NSE signals observed at different positions (A and B) on the PSD are shown in Fig. 6. The phase of the NSE signal at the point A is different from that at the point B, since the field integral along the neutron path is different. If we had observed the NSE signal using a large detector which is not position-sensitive, the NSE signal would have disappeared as a result of the sum of the different phase signals. We can observe each NSE signal, that has a different phase corresponding to the different field integrals, by means of the PSD which specifies the different divergent neutron paths. The use of PSD loosens the condition of the homogeneity of the field integral $D$. Therefore, we can use the scattered neutrons with large angular divergences for the NSE experiment using the PSD.

![Fig. 6](Image)

**Fig. 6** The NSE signals observed at different positions A and B on the PSD as shown in Fig. 5

**ACKNOWLEDGEMENTS**

We are very much indebted to Prof. Y. Ito, Prof. H. Yoshizawa, Prof. Y. Yamada and Prof. Y. Fujii at ISSP, University of Tokyo, Japan for their supports to the construction of the NSE spectrometer and to Dr. C. M. E. Zeyen at ILL, Grenoble, France and Prof. Y. Yamaguchi at IMR, Tohoku University, Sendai, Japan for valuable advices to the design of the NSE spectrometer.

**REFERENCES**

PRACTICAL CONDITIONS IN THE NEUTRON DIFFRACTION UNDER HIGH PRESSURE

Kazuo KAMIGAKI and Masayoshi OHASHI
Institute for Materials Research
Tohoku University, Sendai 980, Japan

Abstract
Practical analysis is made on some conditions in utilizing neutrons for the study of atomistic structure of materials under high pressure. Investigation is made on the geometrical conditions; size of the specimen, width of slits, and the rate of extra-scattering. Experiments are performed on the effects of absorption by high pressure cell and the disturbance due to an overlapping of diffraction peaks. An observation is presented on the pressure-induced transformation in RbBr.

1 Introduction
Neutron diffraction is a powerful tool for the atomistic study of materials under high pressure. In the high pressure works, materials are contained in a thick cell and isolated from visual observation. The situation was improved by utilizing the diamond anvil cell, but the application is made chiefly in the optical property or the X-ray diffraction. Most of the materials are rather transparent for thermal neutrons, and the observation of materials sealed under high pressure is not so difficult if the neutron beam is used as a probe.

However, some difficulties must be conquered to realize a reliable observation. There are some specialities in the neutron diffraction under pressure: the existence of the pressure cell and the pressure transmitting medium. Materials around the specimen cause extra-scattering and contamination of extra-lines in the pattern. Absorption of thermal neutrons by the cell causes the reduction of the peak-height. All such effects act to reduce the quality of the experiment. Incoherent alloys such as Ti-Zr alloy make no coherent peaks and cause a flat background [1, 2], but the absorption is not so small.

Both the angle dispersive method and the energy dispersive or time-of-flight (TOF) method are used for the diffraction experiment. In the former, both the incident beam and the scattered beam scan a range of angle around the specimen, a large volume of materials surrounding the specimen is swept by the neutron beam, and the effects of the extra-scattering become large [1]. The geometry of neutron beams is fixed in the latter, and the design of the apparatus will be rather simple.
2 Geometrical considerations

2.1 Signals from the specimen

Let the neutron beam is applied to a polycrystalline specimen of cylindrical form with diameter $d$, the scattered intensity will be proportional to the number of reflecting planes contained in the specimen, or to the diameter $d$. The rate of absorption by the specimen is proportional to $\exp(-\mu d)$, where $\mu$ is the linear absorption coefficient. The resultant intensity, $d \exp(-\mu d)$ is maximized with respect to $d$ when $d = 1/\mu$, or the diameter equals to the inverse of the linear absorption coefficient.

2.2 Width of neutron beams

The diffracted neutron beam is contaminated frequently with extra-scattering originated from the materials surrounding the specimen. Such contamination is reduced by using slits to limit the irradiated area outside the specimen, and to limit the visual field of the detector. The geometry of diffraction is shown in Fig. 1, where the widths of incident

![Figure 1: Geometry of diffraction.](image)

beam $w_i$ and aperture of the detector $w_d$ are same and $w$, diameter of the specimen is $d$, and the diffraction angle is $2\theta$. Materials contained in the width $w_i$ scatter the neutron beam, and the portion of the scattered beam contained in the aperture $w_d$ is caught by the detector. Hence, a part of materials contained in the rhombus $ABCD$ in Fig. 1 contributes to the diffraction. If the rhombus is perfectly included in the specimen, and if the other materials are not contained in that area, no contamination will be observed in the diffraction pattern. Diagonals of the rhombus are $D_{AC} = w/\sin \theta$ and $D_{BD} = w/\cos \theta$, and $D/w$'s vary with $2\theta$ as shown in Fig. 2. If the width of slits is taken as $w = d\sin \theta$, $(2\theta \leq 90^\circ)$, or $w = d\cos \theta$, $(2\theta \geq 90^\circ)$, $w$ varies with $2\theta$ as $0.13d$ at $15^\circ$, $0.5d$ at $60^\circ$, and the maximum width $0.7d$ is reached at $90^\circ$. In these cases, the rhombus is perfectly included in the area of the specimen, and no contamination will be expected.

2.3 Contamination of the extra-scattering

The extra-scattering will be proportional to the partial area of the rhombus at the outside of the specimen. In the geometry shown in Fig. 1, this part is the shaded area $AEF$, nearly equal to $\Delta AEF$, or $(D_{AC} - d)^2\tan \theta/8$. The ratio $R$ of the sum of two shaded
areas to the part of rhombus included in the specimen is $R = 1/((D/(D - d))^2 - 1)$, where $D \equiv D_{AC}, D_{BD} > d$. If the scattering amplitude of the material at the shaded area is same with that of the specimen, the above expression represents the rate of the extra-scattering. The value of $R$ is shown in Fig. 3 as a function of $D/d$.

In the figure, if $D$ is less than $2d$, $R$ is less than $1/3$. In comparison with Fig. 2, if $w = d/2$, the condition for $1/3$-contamination is $D = 2d = 4w$, or allowed range of $2\theta$ is $30^\circ - 150^\circ$. The nature of the extra-scattering contained in the pattern will be characterized by its intensity and the disturbance due to superposition to the original lines of the specimen. If extra-lines do not coincide with principal lines and subtracted by a conventional way, the pattern will be analyzed clearly.[4]
3 Experiments and discussions

Experimental results and discussions are given here on some effects of absorption and scattering of neutron beams, the effects are caused frequently by materials surrounding the specimen. For the transmission of pressure, ideal conditions required for the medium are to keep the non-crystalline state and to contribute no coherent peaks in the diffraction pattern. Helium gas will be the best in this point of view, but some liquids as alcohols or water are used for the convenience of handling.

As materials for the high pressure cell, high strength steels such as maraging steels are preferable to reach higher pressures. Some aluminum alloys are useful because of its low absorption for thermal neutrons. Diamond, sapphire [3] or some sintered ceramics will be useful, these materials are very hard.

The aim of the present experiments is to obtain fundamental data for the discussion of the effects mentioned above. In the experiments, powdered NaCl is enclosed in a steel cell with various thickness and the diffraction pattern of the system is observed. In this way, relations are obtained between the height of peaks from the specimen with the thickness of the steel wall. The diffractometer is the double axis diffractometer TOG, installed in

![Diagram](image)

Figure 4: Arrangement of the experimental system.

JRR-3. NaCl of 99.3% pure is powdered and enclosed in an aluminum capsule, 12 mm diameter and 0.5 mm thick, and inserted into the cell of thickness $t$ as shown in Fig. 4. No pressure transmitting medium is used and no pressure is applied. The cell is made of low-carbon steel contained with 0.1% C and 0.3% Mn, and the properties for the neutron beam will be almost same with pure iron. The thickness $t$ of the cell is 1.5, 3, 6 and 12 mm, and the thickness $2t$ of the absorber is 3, 6, 12 and 24 mm, respectively. Long collimators made of boron-plastics are attached to the original ones. In this way, geometry of the beam is improved to approach ideal conditions and the background scattering is reduced remarkably.

Diffraction patterns for NaCl and Fe are shown in Fig. 5, some peaks appear at the same lattice spacing: (220)NaCl with (110)Fe and (400)NaCl with (200)Fe, and these peaks are not used in the analysis. The intensity of peaks (111), (200), (311), and (222) in NaCl is plotted in Fig. 6. The logarithm of the intensity decreases almost linearly with the thickness of iron. The rate of decrease is nearly parallel with the absorption of
thermal neutrons in iron shown by a broken line (Fe) in Fig. 6. Therefore, the decrease of the intensity of diffraction peaks is due to the absorption of neutrons by the steel cell. As discussed in the previous sections, the contamination of Fe-lines will be suppressed by a strict alignment in the geometry of beam lines. However, the coherent peaks are very strong, and perfect suppression of contamination is almost impossible in practice. A result of similar experiment done on an aluminum cell with 12 mm thick is shown for (111) by a triangle in Fig. 6. Reduction of intensity is comparatively small even the thickness is large. The absorption in aluminum is shown as a broken line (Al) in Fig. 6, the line is parallel with the above result.

If aluminum alloys are used for the pressure cell, absorption of thermal neutron is considerably small and intense peaks will be obtained in the diffraction pattern. On the other hand, the pressure attained will be limited to as high as 1 GPa. Ti-53wt% Zr alloy has no coherent peaks for thermal neutrons but its mechanical strength is not so high, and the pressure will be limited to about 1.5 GPa. Higher pressures as 3 - 5 GPa are attained by steels, but the intensity of peaks is reduced considerably. To overcome such weak points, some improvements must be applied for the intensity of the source, the efficiency of detection, and the reduction of background, etc. Some of them are out of range of our personal effort, but their importance must be remembered.

Diffraction patterns for Al and KCl are shown in Fig. 5. In KCl, the overlapping of lines with Fe or Al is less than in NaCl. An appropriate combination of materials must be investigated in accordance with the purpose of the experiment.
4 Pressure-induced transformation in RbBr

4.1 High pressure apparatus

A piston-cylinder type high pressure apparatus was designed for the angle dispersive neutron diffraction. The material of the cell was Ti-53wt%Zr alloy. No coherent scattering of the cell is observed in this composition. The alloy was made by arc-melting the raw metals 97% pure, and formed by the lathe in a cylinder: 3 cm outer diameter, 0.8 cm hole diameter, and 10 cm long. Both ends of the cylinder were inserted into steel binding rings. Pistons were made of tungsten carbide. Powdered specimen of RbBr 99.3% pure mixed with one half of KCl was enclosed in a thin-walled capsule made of teflon, CS$_2$ was used as the pressure-transmitting medium.
4.2 Neutron diffraction on RbBr

The experiment was made on TOG diffractometer in JRR-3, neutron wavelength was about one angstrom. A diffraction pattern obtained at 1 bar is shown in Fig.7. All lines are indexed with two NaCl-type compounds: RbBr and KCl, no overlap of peaks is observed. With increase of pressure, peaks shift to higher angle side in correspondence with volume contraction. Applied pressure is estimated in comparison with results on KCl obtained by Vaidya and Kennedy [6]. The diffraction pattern obtained at 7.5 kb is shown in Fig. 8. The pattern for KCl is keeping the NaCl-type, however, in RbBr all lines are indexed with the CsCl-type structure. This transformation was observed at about 4.5 kb and accompanied with a volume contraction of -15 %. [2]
4.3 Discussion of the results.

In Figs. 7 and 8, all lines are originated from specimens, and no extra-line is observed. However, the background scattering appears in a considerable amount in comparison with ordinary experiments. Most of the background is composed of incoherent scattering from Ti-Zr alloy. In the disordered system as disordered alloys or liquids, a wavy pattern due to the atomic correlation is observed. Such pattern was reported in the experiment using Ti-Zr cell at ILL [5], analysis of the background must be made carefully. The next problem is the absorption of neutron beams by the cell. The absorption is very small in Zr, but large in Ti. The atomic concentration of Ti is very large in the alloy, the resultant absorption coefficient is about $1 \text{ cm}^{-1}$, and the effect of absorption is not so small.

The conditions analyzed in the present report will be useful for execution of diffraction experiments under high pressure. Accumulation of practical efforts will result in a steady progress, and the evaluation of neutron beam as an atomistic probe will be improved.

5 Acknowledgement

The authors wish to express their thanks to Prof. Yasuo Yamaguchi for his advices.

References

NEUTRON SCATTERING CROSS SECTIONS OF LIQUID HYDROGEN AND DEUTERIUM FOR COLD NEUTRON PRODUCTION

Nobuhiro MORISHIMA and Daisuke MIZOBUCHI
Department of Nuclear Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606, Japan

ABSTRACT

The double-differential and total cross sections for neutron scattering from liquid hydrogen and deuterium at temperatures between the melting and boiling points are calculated. It is based on a generalized cross-section model describing properly the molecular motions in the liquids in terms of individual translations and intermolecular correlations. Intramolecular motions such as the nuclear spin correlations, free rotations and harmonic vibrations are also included similarly to the Young–Koppel model. The results of numerical calculations agree very well with a variety of the experimental cross-section results, both double-differential and total, at different temperatures and in different ortho–para contents over a wide range of incident neutron energies. Furthermore it is shown that the velocity autocorrelation functions inherent in the liquids are determined successfully.

INTRODUCTION

Liquid hydrogen and deuterium are both important as materials to produce intense cold-neutron beams from reactors and accelerators, because they have some favourable properties of neutron slowing down such as low atomic mass, adequate scattering cross section and molecular motions below low boiling point. The available experimental data on neutron cross section are, however, not sufficient to reproduce or tabulate scattering processes at low energies\(^\text{1-3}\). Hence one relies on cross-section models to predict the relevant data. Several models have been developed for evaluating the interaction of neutrons with the molecules moving about in the liquids\(^\text{4,6,8}\), as a generalization of the Young–Koppel(Y–K) model derived for a dilute gas of molecular hydrogen and that of molecular deuterium\(^\text{9}\). Major idea is to replace the free translations by the superposition of molecular motions in the diffusive and solid–state modes. Such improvement is superior to a free-gas treatment, but the significant deviations from the experimental results still remain.

In the present model, the molecular motions in the liquids are taken into account properly in terms of short–time free translations, long–time diffusion with viscosity and short–lived vibrations due to intermolecular forces. For the intramolecular motions, the spin correlations, free rotations and harmonic vibrations are included similarly to the Young–Koppel model. The present model is therefore applicable to predict the neutron scattering from both liquids at all temperatures between the melting and boiling points over a wide range of neutron energies, say 0 to 10 eV. This is verified by the good agreement with a
variety of the experimental results: (a) The double-differential cross sections of the liquid hydrogen with the ortho–para ratio of 3:1 at 15, 18 and 21 K for 2.9 meV neutrons\(^3\), the liquid hydrogen with 41 % ortho and 59 % para at 19.8 K for 21.8 and 87 meV neutrons\(^2\), and the liquid deuterium with the ortho–para ratio of 2:1 at 20 K for 2.9 meV neutrons\(^3\). And (b) the total cross sections of the liquid hydrogen with the ortho–para ratio of 3:1 at 16 K, the para–hydrogen at 14 K and the normal–deuterium at 19 K over the energy range of 1 to 100 meV\(^3\). In consequence of the present modeling, the velocity autocorrelation functions for the molecular motion in the liquids are determined successfully. It appears that the over–all shapes of the results represent fairly well the true ones in view of the good reproduction of the relevant double differential cross sections.

**CROSS SECTION MODEL**

There are two features which we have to consider in the development of the cross section model. The first one is the coherent (i.e. interference) scattering from different molecules of para–hydrogen with total spin \(S=0\) and deuterium in para–state \(S=1\) and in ortho–state \(S=0,2\). Note that an ortho–hydrogen molecule with \(S=1\) is an incoherent scatter. And second there is the molecular motions inherent in the liquid phase, thus causing quasi–elastic scattering for cold neutrons and up–scattering for lower energy neutrons. Owing to these two features, we have to take account of the intermolecular motions in the liquids properly.

In the present model, the molecular motions are described by the convolution of the static structure factor \(S_c(\kappa)\) and the self scattering function \(S_0(\kappa,\omega)\) where \(\kappa\) and \(\omega\) are the wave number and the angular frequency, respectively. Since \(S_c(\kappa)\) represents the spatial configuration of molecular centers in wave–number domain, the one calculated exactly from the hard–sphere model\(^6\) is utilized. The adequatness of such \(S_c(\kappa)\) is checked by the comparison with the experimental result \(S_c(\kappa)\)\(^9\) corrected for molecular form factor and orientational correlation. It is found that \(S_c(\kappa)\) is in close agreement with \(S_c(\kappa,\omega)\) at small values of \(\kappa\) near the first peak.

For the calculation of \(S_c(\kappa,\omega)\) representing the individual motions of molecules in the liquids, we follow a familiar theory\(^{10}\) by which \(S_c(\kappa,\omega)\) is given by the Fourier transform of the intermediate scattering function \(F_s(\kappa, t)\) and in the Gaussian approximation \(F_s(\kappa, t)\) is expressed in terms of the width function \(W(t)\) and basically the velocity autocorrelation function \(C(t)\). Hence, forming \(C(t)\) or its Fourier transform \(g(\omega)\) being called a frequency spectrum, we can calculate \(S_c(\kappa,\omega)\). In the present modeling, the following modes of molecular translational motions are incorporated into \(g(\omega)\).

(a) The long–time diffusion associated with viscosity, which is expressed in terms of a \(\sqrt{\omega}\)–like characteristic at \(\omega\rightarrow 0\)\(^{10}\) and \(g(0)=MD(T)/\pi k T\) where \(N\) is the molecular mass, \(D(T)\) the temperature–dependent diffusion coefficient, \(k\) the Boltzmann constant and \(T\) the absolute temperature.

(b) The short–lived vibrational motion due to the intermolecular forces\(^1\) of which the frequency spectrum is deduced from neutron scattering results \(g^v(\omega)\) for liquid ortho–hydrogen at 14.7 K\(^{13}\). Since the total area of \(g^v(\omega)\) has been found to be 0.7, not equal to the correct value of unity, it is assumed that \(g^v(\omega)\) is reliable in gross shape, rather than in fine structure and magnitude.

(c) The short–time free–gas like translations, which are embodied in the calculation of \(W(t)\) by the substitution of imaginary time yielding a correct recoil effect for classical time.
(d) The temperature dependence of the molecular motions in the liquids, which is incorporated directly through the diffusion coefficient $D(T)$ and the viscosity coefficient $\nu(T)^{13}$ and also by the optimum selection of the values of some free parameters involved in $g(\omega)$. The two criteria for the optimization are taken: the normalization of the total area of $g(\omega)$ to unity at all the temperatures of our interest; and the similarity of the calculated incoherent cross sections with the experimental ones for liquid hydrogen$^2$.

Figure 1 shows a typical result of $g(\omega)$ for liquid hydrogen at 14.7 K, together with $g'(\omega)$. Also shown in Fig. 1 by the dashed curve is the fitted result to $g''(\omega)$. It is the initial guess used for the determination of $g(\omega)$, then corrected to $g(\omega)$ given by the solid curve. It may be worth noting that the peak components appearing in $g''(\omega)$ at $\omega = 15$ rad/psec are not included into $g(\omega)$, since such frequency components have not produced significant improvement in the cross-section results.

Consequently, using the $S_0(\kappa)$ and $S_0(\kappa,\omega)$, we can calculate the interference scattering from liquid hydrogen and deuterium. For the intramolecular motions, the Young–Koppel model is adopted as it is: nuclear spin correlations as ortho and para states, free rotations in view of slight hindrance due to quadrupole–quadrupole interaction$^{14}$ and harmonic vibrations valid for low levels near the ground state. Hence we can write the double–differential cross section (per atom) applicable to the case of the nuclear spin $I$ and the molecular spin $S$:

$$\frac{d^2\sigma}{d\Omega d\epsilon} = \frac{1}{2\hbar^2 k_0} \sum_{j,j'} \frac{S_j(\kappa,\omega \omega') P_{j'j} (2J' + 1) \exp \left( -\frac{k_0^2}{4M\omega} \right)}{n_{j'j} \epsilon_{j'j}} \sum_{\lambda \lambda'} \frac{1}{n_{\lambda \lambda}} |A_{\lambda \lambda}|^2 C(JJ' I:00)^2$$

$$+ \frac{1}{2\hbar^2 k_0} \sum_{j,j'} \frac{S_j(\kappa,\omega \omega') P_{j'j} (2J' + 1) \exp \left( -\frac{k_0^2}{4M\omega} \right)}{n_{j'j} \epsilon_{j'j}} \sum_{\lambda \lambda'} \frac{1}{n_{\lambda \lambda}} |A_{\lambda \lambda}|^2 C(JJ' I:00)^2,$$  \hspace{1cm} (1)

where

$$S_j(\kappa,\omega \omega') = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp \left( i\omega t \right) \exp \left( -k^2 w(t) \right) \exp \left( i\omega t / \hbar \right) dt,$$  \hspace{1cm} (2)

$$w(t) = \frac{k}{\hbar} \int_0^t \omega^2 (1 - \cos \omega t) g(\omega) d\omega,$$  \hspace{1cm} (3)

$$g(\omega) = g(0) \left\{ \epsilon \exp \left( -\omega / \omega_0 \right) + (1 - \epsilon) \exp \left( -\omega / \omega_0^2 \right) \right\} + A(\omega / \omega_0)^2 \exp \left( -\omega / \omega_0^3 \right),$$  \hspace{1cm} (4)

with $k, k_0$ = wave numbers of incident and scattered neutrons.
\( \alpha_c, \alpha_t \) = coherent and incoherent scattering length, 
\( m, \alpha \) = atomic mass and bond length, 
\( J \) = quantum number of initial rotational state to be even for para-hydrogen and ortho-deuterium, and odd for ortho-hydrogen and para-deuterium, 
\( J', J'' \) = quantum numbers of final rotational states having, respectively, the same and opposite parity with \( J \), 
\( n \) = quantum number of final vibrational states, 
\( A_d = \int_{\mu}^{1} \exp (-\frac{\kappa^2 \mu^2}{\delta m \omega} + i \kappa \alpha \mu / 2) P(\mu) d\mu, \) \( \text{(5)} \)
\( C(J,J',0) \) = the Clebsch–Gordan coefficient, 
\( P_{JS} \) = statistical weight of the state \( J \) with spin \( S \), 
\( \alpha = \left\{ \begin{array}{ll}
(2\hbar^2/m\alpha^3)\{J(J+1)-J(J-1)} / 2 + n\hbar \omega \text{ for } S_{s}(K,\omega') \\
0 \text{ for } S_{s}(K,\omega)
\end{array} \right. \) \( \text{(6)} \)
\( \varepsilon, \omega_1, \omega_2, \omega_3 \) = parameters determined by the above requirements (a)–(d), 
\( A \) = constant to normalize the total area of \( g(\omega) \) to unity.

It should be noted that the numerical calculations of the cross section are carried out using the fast and accurate procedure for evaluating continuous Fourier integrals, since an ordinary FFT algorithm based on a trapezoidal rule of integration is not efficient for the requirement of both accuracy and computation time.

**RESULTS AND DISCUSSION**

Owing to the diffusive motions of molecules in the liquids, cold neutrons are scattered quasi-elasically. Figure 2 shows this behavior by the double-differential cross sections for 2.9 meV neutrons from the liquid hydrogen at 21 K with the ortho:para ratio of 3:1. Diffusive broadening of the quasi-elastic peak is well reproduced for all the scattering angles of 20°, 45° and 90°, where the calculated results have been corrected for the instrumental resolution with the Gaussian

---

**Fig. 2.** Double-differential scattering cross sections.
form in flight time. Also shown in Fig. 2 is the up-scattering peak in the vicinity of 14.5 meV, due to the transition of rotational level \( J = 1 \) from ortho-hydrogen \((J=1)\) to para-one \((J=0)\).

As the liquid temperature approaches to the melting point, the effect of viscosity as well as the vibrational motion becomes dominant, while the magnitude of \( D(T) \) decreases significantly. This is reflected on the double-differential cross sections at 15 K in which the quasi-elastic peaks are narrow and sharp, compared with those at 21 K in Fig. 2. The cross-sections at 18 K are also analyzed and found to indicate middle spectra between those at 15 and 21 K.

For larger energies of incident neutrons, the short-lived vibrational motion become significant. Figure 3 shows the double-differential cross sections for 21.8 meV neutrons from the 41-% ortho-hydrogen at 19.8 K. A greater and asymmetric broadening of the quasi-elastic peak arises largely from the vibrational motion characterized by the peak spectrum of \( g(\omega) \) in the vicinity of 8 rad/ps. Such spectral characteristics are essential for liquid hydrogen and hence hardly expressed in terms of the superposition of frequency components in the solid-state and diffusive modes. This is the reason that the gentle broadening of the peak has not been explained properly so far. Concerning the results in Fig. 3, two remarks are further noted. The transition from para- to ortho-hydrogen appears as a small down-scattering peak at 6 meV. And the experimental results are presented after having been multiplied by a factor of 0.71. Such an adjustment is made in view of the fact that the present model yields the correct magnitudes of total cross section at 21.5 meV and other energies.

When incident neutron energies are much higher than the intermolecular binding characterized by a Debye temperature of the order of 8 meV, we consider the liquids to be almost molecular gas. This can be seen from Fig. 4 where the double-differential cross sections for 87 meV from the 41-% ortho-hydrogen at 19.8 K are presented \(^3\). Note that the experimental results are adjusted using the same factor as in Fig. 3. The calculated results agree...
very well in shape and position with the experimental ones, while the Young–Koppel model yields narrower and larger peaks, especially for smaller scattering angles. This means that the incident energy of 87 meV is not sufficiently high to assume the molecular translations to be completely free. The vibrational and diffusive motions are still effective, in addition to the gas-like translations of molecules causing a major down-scattering.

One feature to be noted is the quantum effect due to the zero-point motion of a hydrogen and a deuterium molecule, which is estimated as a temperature increase of $\delta T = 10.5$ and 9.5 K, respectively, in view of the corresponding magnitudes of He and Ne. Replacing the liquid temperature $T$ by the effective temperature $T + \delta T$, we can incorporate the quantum effect into the model. The results are shown in Fig. 4 by the dashed curves, which are much closer to the experimental results.

As to the liquid para-hydrogen and the liquid deuterium, coherent scattering is dominant for low neutron energies below about 10 meV. Figure 5 shows this interference effect in terms of the double-differential cross sections for 2.9 meV neutrons from liquid deuterium with the ortho-para ratio of 2:1 at 20 K. Since the experimental results have been presented in a relative magnitude, one of them at 20° is normalized to the corresponding result of the calculation. Two major features are observed. The magnitudes of the quasi-elastic peak for the smaller scattering angles are suppressed by the asymptotic slope of $S_0(\kappa)$ at small values of $\kappa$. On the contrary, for the larger scattering angles, the position of the quasi-elastic peak is shifted towards the up-scattering side on account of the steep increase in $S_0(\kappa)$ near the first peak. This means that the calculated results are very sensitive to the shape of $S_0(\kappa)$. It can also be seen from Fig. 5 that there is the overall agreement between the calculated and experimental results, though the up-scattering peak at 7.5 meV, due to the para to ortho transition, is poorly estimated. Further improvement may be obtained by other approaches to the proper description.
of coherent inelastic scattering from collective motions.

Finally, in order to check the integral properties of the present model, a total cross section is calculated numerically for both the liquids at many different temperatures and ortho–para contents. Some of them are compared with the experimental results\(^3\) for normal hydrogen at 16 K and para–hydrogen at 14 K in Fig. 6, and normal–deuterium at 19 K in Fig. 7. Note that the latter experimental result is not assigned to any mixture of ortho– and para–D\(_2\), so that it is assumed to be the normal one with the ortho–para ratio of 2:1. Obviously, very good agreement is obtained in the absolute unit of barn per atom. Several remarkable features are summarized as follows: (a) A sudden rise in the para–hydrogen cross section at about 15 meV, due to the para to ortho transition. (b) A diffuse Bragg edge in the para–hydrogen and the deuterium cross section in the vicinity of 3 meV, originating from the intermolecular interference through \(S_e(k)\). (c) An asymptotic approach to the free–atom cross section of 20.4 barn for H and 3.4 barn for D. (d) A uniform increase with decreasing neutron energies far below 1 meV, causing up–scattering of neutrons by the thermal motions of liquid molecules and the transition of ortho– to para–hydrogen. (e) Slight deviations in the deuterium cross sections at about 1.5 meV, which may be improved by other approaches to treat coherent inelastic scattering, for instance, by a mean field approximation\(^3\).

---

Fig. 5. Double-differential scattering cross sections.

Fig. 6. Total cross sections.
CONCLUSION

In view of the very good agreement with the available experimental results, we conclude that the present cross-section model can predict properly the neutron scattering from liquid hydrogen and deuterium at all temperatures between the melting and boiling points over a wide range of neutron energy, say 0 to 10 eV. Hence the present model can be utilized as a data base for the design and analysis of advanced cold-neutron sources.

It is also shown that the velocity autocorrelation functions inherent in the liquids are determined successfully. They are expected to be verified in near future by neutron scattering and/or molecular dynamics.

REFERENCES

High Pressure Apparatus for Neutron Diffraction Study

*Gendo OOMI and *Yôichi SHIOZAKI

*Department of Physics,  
Faculty of General Education, 
Kumamoto University, Kumamoto, 860 Japan

*Department of Physics,  
Hokkaido University, 
Sapporo, 060 Japan

ABSTRACT

High pressure apparatus for neutron diffraction study has been designed by using barrel-shaped aluminum alloy. The diffraction profile of thiourea SC(NH₂)₂ was examined at ambient pressure and 4.5 kbar² at room temperature. It was confirmed that the present high pressure apparatus can be used to get a good diffraction profile at high pressure up to at least 10 kbar.

INTRODUCTION

Neutron diffraction (ND) technique is a good tool to study the phase transition of the condensed matters such as metals, alloys, dielectrics and so forth. Many kinds of interactions which dominate the phase transition are well known to depend on pressure or a change in volume. The combination of these two techniques, the pressure and ND, is expected to give a useful information for the study of the mechanism of phase transition in the condensed matters.

So far several high pressure apparatus have been designed for ND experiments. High pressure cells below 10 kbar are made of aluminum alloy [1,2] and above 10 kbar of high strength alumina (Al₂O₃) [3-5]. In the diffraction experiments at high pressure, the diffraction lines from high pressure cell sometimes mask the lines from the samples. To avoid the difficulty it is better to use the high pressure ND cell which is made of a material having simple crystal structure.

Many dielectric substances show structural phase transition below 10 kbar and large effect of pressure on the phase transition temperature, which reflects that the dipole interaction in these materials is strongly dependent on pressure or a change in volume. Thus we expect to get a useful and important information about the fundamental aspects
of the phase transition in the dielectrics in the pressure range $P < 10$ kbar.

In the present work we made an attempt to make a high pressure apparatus for ND experiment below 10 kbar, in which we can carry out the electrical measurement simultaneously. The details of ND high pressure cell will be described in the following section and an example of the measurement of diffraction profile of thiourea is also indicated.

EXPERIMENTAL PROCEDURE

[1] Design of high pressure apparatus

The high pressure in the present work was generated basically by means of piston and cylinder method. Figure 1 shows the exploded view of the present high pressure apparatus. The cylinder (5) was made of a barrel-shaped aluminum alloy (7075-T6 Kobe Steel Co. Ltd.) which was tightened by two steel support pieces (4).

![Exploded View of High Pressure Apparatus](image)

Cu-Be alloy
hard aluminum
stainless steel

Figure 1 Exploded view of the high pressure apparatus designed in the present work: (1) locking screw to clamp pressure, (2) WC piston, (3) locking screw for support ring, (4) stainless steel support ring, (5) tapered aluminum alloy cylinder, (6) Cu-Be plug, (7) pressure pad and (8) electrical lead.
Figure 2 Central part of the present apparatus in an expanded scale.

Figure 3 Displacement of the piston as a function of load when NH₄F is compressed.

Since the maximum pressure achieved by using Al alloy is about 6 kbar [2], the cylinder (5) must be strongly supported if we use it above 6 kbar. The advantages using Al alloy are, 1) the diffraction profile is relatively simple compared with that of Al₂O₃ cylinder having trigonal structure and 2) it is easy to make a barrel-shaped cylinder.

First the cylinder (5) is forced into the two reinforced support rings (4) which are tightened by two locking screws (3) after compressing by hydraulic press. High pressure cell made of Al having a diameter of 8 mm was pressurized by using tungsten-carbide (WC) piston (2) and hydraulic press. The pressure inside the cell was clamped by two locking screws (1). The details of the cell and the path of neutron are described in an expanded scale in Fig. 2. A manganin wire is placed inside the cell to measure the pressure simultaneously through the experiment. The length of Cu-Be lids is adjusted for the wire not to be irradiated by neutron.

[II] Pressure inside the cell.

In order to estimate roughly the pressure inside the Al cell, NH₄F powder entirely fills up the free space in the cell. In NH₄F several phase transitions are observed at 3.6 kbar (I-II) and 11.6 kbar (II-III) at room temperature [6]. Figure 3 shows an example of the pressure dependent volume change ΔV/V of NH₄F which is related to a change in the displacement of piston, ΔL, such as ΔV/V = ΔL/L. The volume decreases smoothly with increasing the load on the cell but
shows an anomalously large decrease around the load of 30 kg/cm², which corresponds to the I-II phase transition, 3.6 kbar. After a compression up to 80 kg/cm², it was found that no deformation of the cylinder and no cracks in the piston and cylinder were observed. So the present high pressure apparatus can be used up to at least 10 kbar at room temperature. The ND experiment was carried out by using JRR-3. The amount of specimen (thiourea) was about 1.4g. The profile was observed at room temperature in the range of 2θ, 18° < 2θ < 82° by step scanning method of an interval of 0.1°.

RESULTS AND DISCUSSION

Thiourea, SC(NH₂)₂, is a particularly interesting example in that it demonstrates the advantage of combining pressure measurements with those of other variables such as temperature and electric field. At room temperature it shows several phase transition as pressure increases: it is paraelectric at ambient pressure, but transforms into superstructure having three times larger period in the c-axis than in the para-phase (c = 3 c₀) [7].

Figure 4 shows the diffraction profile of high pressure apparatus without any specimen. The lines from (111) and (200) of Al alloy were clearly observed around 2θ = 62° and 73°. Since there are no diffraction lines between 18° and 61°, the lines of specimens in this 2θ range are not masked by those from the high pressure apparatus.

Figure 4 Neutron diffraction profile of the present high pressure apparatus without any specimen.
Figure 5 Neutron diffraction profile of thiourea and the apparatus. Some lines indicated by arrows are from NH₄F.

The ND profile of SC(NH₂)₂ at about 4.5 kbar is shown in Fig. 5 including the diffraction pattern from pressure vessel. Four lines of the specimen are observed clearly at room temperature. The background of the profile becomes higher than that in Fig. 4, which is due to the hydrogen atom in thiourea. Because we didn't observe the enough number of diffraction lines to confirm the superstructure, it was difficult to perform the detailed analysis at present. But it is confirmed that the present high pressure apparatus is suitable for the ND experiment up to at least 10 kbar. Further systematic investigations, particularly at low temperatures, are highly desired.

References

POLARIZED THERMAL NEUTRON FIELD AROUND POLARIZED HELIUM-3 GAS CELLS IN A NUCLEAR REACTOR

Kenichi ISHIKAWA, Tetsuo IGUCHI and Masaharu NAKAZAWA

Department of Nuclear Engineering, Faculty of Engineering
University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo, 113 Japan

ABSTRACT

A Monte Carlo simulation study was made on the production of polarized thermal neutron field using polarized \(^3\)He gas cells as neutron spin-filters in a nuclear reactor. First, the spin-dependent neutron transport equation was formalized by introducing the projection of neutron spin into the phase space of neutron state. Second, Monte Carlo calculations were carried out on the neutron polarization and flux around polarized \(^3\)He gas cells in graphite moderators, where monoenergetic approximation was used and spin flip in scattering was taken into account. The results indicate that highly polarized thermal neutron field can be obtained efficiently by inserting polarized \(^3\)He gas cells into the current thermal neutron field in the graphite column, instead of using the cells in neutron beam lines outside reactors or accelerators.

1. INTRODUCTION

The polarization of the nuclear spin of \(^3\)He is of interest from several perspectives. It has recently been recognized that polarized \(^3\)He is one of the best filter to polarize slow s-wave neutrons with energy less than 1eV\(^1\). \(^3\)He nuclei absorb neutrons through a very strong resonance absorption reaction with the cross section greater than a thousand barns. The spin of the resonance state(compound nucleus) is zero while that of a neutron and \(^3\)He nucleus is 1/2. This absorption reaction, therefore, occurs only when spins of a neutron and \(^3\)He are anti-parallel. When the neutron beam passes through a polarized \(^3\)He target, only neutrons with the spin direction anti-parallel to that of a polarized \(^3\)He are absorbed selectively, and a polarized neutron beam is obtained as shown in Fig. 1. The neutron scattering cross section of \(^3\)He is negligibly small, which is a favorable feature for a neutron polarizer.

Suppose that polarized \(^3\)He gas cells are inserted into a nuclear reactor. Then, slow neutrons in the reactor can pass through the cells more than one times since neutrons which have passed through them can be scattered from reactor materials (mainly, from moderators) and directed toward the cells again. Higher neutron polarization, therefore, may be achieved than in the case that a neutron beam is passed through polarized \(^3\)He gas cells (outside a nuclear reactor) just once, if a neutron spin direction is kept unchanged in scattering.

In the present paper we report the results of a Monte Carlo simulation study on the production of a polarized thermal neutron field using polarized \(^3\)He gas cells in a nuclear reactor. In Sect. 2, the method of polarizing \(^3\)He nuclear spin through spin exchange with optically pumped Rb atoms is explained. In Sect. 3, the formalization of the spin-dependent neutron transport equation is presented, and the change of a neutron spin direction in
scattering is discussed. In Sect. 4, the results of Monte Carlo calculations on the neutron polarization and flux obtained are presented and discussed. In Sect. 5 conclusions are given.

![Diagram of a polarized $^3$He filter as a neutron spin filter](image)

**Fig. 1.** Principle of a polarized $^3$He filter as a neutron spin filter

### 2. POLARIZATION OF $^3$He BY SPIN EXCHANGE WITH Rb

The polarization of $^3$He nuclei results from the contact hyperfine interaction between the nuclear spin of $^3$He and the atomic spin of Rb which is polarized by the optical pumping process\(^2\)). This interaction is effective during the brief time of Rb-$^3$He collisions. The time scale for polarization transfer from Rb to $^3$He (≈ 10 h) differs from that for optical pumping of Rb (≈ 1 ms) by seven orders of magnitude.

![Diagram illustrating optical pumping of Rb](image)

**Fig. 2.** Illustration of optical pumping of Rb with the nuclear spin neglected. Dashed arrows correspond to no buffer gas and solid arrows to the presence of buffer gas.
The principle of laser optical pumping of Rb vapor is illustrated in Fig. 2 for which \( j = \frac{1}{2} \) in the ground state. In Fig. 2, the nuclear spin is neglected and the relevant states are the \( s_{1/2} \) and \( p_{1/2} \) states each with two magnetic substrates \( m_s = \pm 1/2 \). The nuclear spin introduces hyperfine splitting of 3036MHz. Incident, circularly polarized laser light with magnetic projection \(+1(\sigma_z)\) can only be absorbed by the \( s_{1/2} \) state with \( m_s = -1/2 \). This populates the \( p_{1/2} \) sublevel with \( m_s = +1/2 \) which decays to either sublevel of the ground state. In the absence of buffer gas collisions which mix the two \( p_{1/2} \) levels, the relative decay rates of the \( p_{1/2} \) state with \( m = +1/2 \) are given by the Clebsh-Gordon coefficients, \( \frac{2}{3} \) and \( \frac{1}{3} \) as shown. However, in a practical target, buffer gas collisions randomize the \( p \) states and the relative decay rates to each sublevel of the ground state are \( \frac{1}{2} \). As a result, two circularly polarized photons must be absorbed in order that a single unit of angular momentum is transferred to the atom. Furthermore, the \( p_{1/2} \) states decay not only radiatively, but also nonradiatively through collisions with the buffer gas, specifically \( N_2 \). The radiative decay rates are negligible compared to the nonradiative quenching rates. Thus, in the absence of any significant relaxation mechanism, almost all Rb atoms will eventually be pumped into the \( s_{1/2} \) sublevel with \( m_s = +1/2 \).

### 3. NEUTRON SPIN IN TRANSPORT

#### 3.1. Spin-dependent Neutron Transport Equation

In usual neutron transport calculations such as nuclear reactor criticality problems and neutron shielding problems, the neutron spin is not taken into account since it is assumed that neutrons are unpolarized. In the contrary, when we treat the neutron transport in a reactor with neutron spin filters in it, calculations must be based on the spin-dependent neutron transport equation.

As well known, the transport equation for unpolarized neutrons is written in terms of the angular flux of neutrons at point \( r \) traveling in the direction \( \hat{\Omega} \) with energy \( E \) and velocity \( v \) at time \( t \), \( \varphi(r,E,\hat{\Omega},t) \), as,

\[
\frac{1}{v} \frac{\partial \varphi}{\partial t} + \hat{\Omega} \cdot \nabla \varphi + \Sigma_i(r,E) \varphi(r,E,\hat{\Omega},t) = \int_{\hat{\Omega}} d\hat{\Omega}' \Sigma_i(E' \rightarrow E,\hat{\Omega}' \rightarrow \hat{\Omega}) \varphi(r,E',\hat{\Omega}',t) + S(r,E,\hat{\Omega},t) \tag{1}
\]

where \( \Sigma_i \) is the total macroscopic cross section for neutrons at position \( r \) with energy \( E \), \( \Sigma_i(E' \rightarrow E,\hat{\Omega}' \rightarrow \hat{\Omega}) \) is the macroscopic cross section for neutrons traveling in the direction \( \hat{\Omega}' \) with energy \( E' \) scattered into the direction \( \hat{\Omega} \) and energy \( E \), and \( S \) is the neutron emission/source density.

The spin-dependent neutron transport equation can be obtained simply by introducing the projection of neutron spin, \( s \), which takes two discrete values \( up(+\frac{1}{2}) \) and \( down(-\frac{1}{2}) \), into the phase space of a neutron state as follows,
\[
\frac{1}{v} \frac{\partial \varphi}{\partial t} + \hat{\Omega} \cdot \nabla \varphi + \Sigma_s(r, E, s) \varphi(r, E, \hat{\Omega}, s, t)
\]

\[
= \sum_{s = \text{up, down}} \int_{E'}^{E'} dE' \int_{s'}^{s'} dE, \Sigma_s(E' \rightarrow E, \hat{\Omega}' \rightarrow \hat{\Omega}, s' \rightarrow s') \varphi(r, E', \hat{\Omega}', s', t) + S(r, E, \hat{\Omega}, s, t)
\] . (2)

It should be noted that cross sections generally depend on the neutron spin direction when neutrons have high energy even if targets are unpolarized.

3. 2. Neutron Spin Flip in Scattering

The present idea to produce highly polarized thermal neutron field in a nuclear reactor is based on the expectation that scattering in a reactor will enable thermal neutrons to pass through $^3$He gas cells several times. It is, therefore, desirable that the spin direction of thermal neutrons are kept unchanged in scattering from materials.

The neutron scattering can be classified into coherent one and incoherent one. It is known that the thermal neutron spin direction is preserved in coherent scattering and one-third of incoherent one and that it is flipped in two thirds of incoherent scattering. Coherent and incoherent thermal neutron scattering cross sections and the probability of thermal neutron spin flip in scattering from several nuclei are summarized in Table 1.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>coherent scattering cross section (barns)</th>
<th>incoherent scattering cross section (barns)</th>
<th>spin flip probability in scattering (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>0.439</td>
<td>20.052</td>
<td>65.2</td>
</tr>
<tr>
<td>$^2$D</td>
<td>2.486</td>
<td>0.904</td>
<td>17.8</td>
</tr>
<tr>
<td>C</td>
<td>4.739</td>
<td>0.007</td>
<td>0.1</td>
</tr>
<tr>
<td>O</td>
<td>3.759</td>
<td>0.002</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 1 indicates that spin flip probability for thermal neutrons in scattering from light water or heavy water is relatively large and that high thermal neutron polarization cannot be obtained in a reactor with them as moderators or coolants. In contrary, the thermal neutron spin is hardly flipped in scattering from carbon. This leads to the conclusion that it is desirable to use graphite as a moderator instead of water in a reactor so as to get high thermal neutron polarization.

4. MONTE CARLO CALCULATIONS

4.1. The Basic Concept of the Present Idea

The basic concept of the present idea is shown schematically in Fig. 3. The reactor is divided roughly into two layers, the source area and the polarizer area. The former contains nuclear fuel, moderators (made of graphite), control rods, reflectors etc. like normal nuclear reactors. The latter is peculiar to the present idea and contains graphite which scatters thermal neutrons with rare spin flip and polarized $^3$He gas cells which polarize neutrons. (It should be noted that Monte Carlo calculations shown in the following subsections were carried out on a spherical-shaped reactor, not on a cylindrical-shaped reactor as shown Fig. 3, for simplicity.)
4. 2. Effect of the Location of Polarized $^3$He on the Thermal Neutron Polarization

We have studied the neutron polarization in the center of a reactor containing one layer of polarized $^3$He gas. The scattering, moderation, diffusion, etc. of neutrons have long been studied in reactor physics, and a huge amount of information on the cross sections of neutrons of energy range between 25meV and 20MeV has been accumulated into the nuclear data e.g. ENDF/B, JENDL. These data, however, cannot be used directly in the present study since they do not contain the information on spin-dependent neutron cross sections whereas fast neutron cross sections are generally spin-dependent. Thus, a complete Monte Carlo calculation of spin-dependent neutron transport is not feasible at the present stage.

In the present study, therefore, we have used monoenergetic approximation since it is polarized thermal neutron field that we are interested in. Let us consider a spherical-shaped reactor containing one layer of polarized $^3$He gas as shown in Fig. 4. The source area in this figure is an isotropic surface neutron source. It emits monoenergetic thermal neutrons isotropically. The polarizer area is divided into three layers. The outer layer and the inner layer consist of graphite. The middle is 1cm-thick $^3$He gas layer. The density and polarization of $^3$He gas are $1.66 \times 10^{20}$ cm$^{-3}$ and 80% respectively.

We calculated the thermal neutron flux and polarization in the center of this simplified reactor taking into consideration neutron spin flip in scattering as noted in Subsect. 3.2. Fig. 5 shows the results as a function of the location of $^3$He gas layer. It should be noted that when thermal neutrons once pass through a $^3$He gas layer of the same thickness, density and polarization as in Fig. 4 the polarization of 55.9% is obtained (Let us call this one-pass polarization). Fig. 5 indicates that higher neutron polarization can be obtained in the center by inserting $^3$He gas layer into a reactor and utilizing the scattering from graphite. Especially, when $^3$He gas layer is located at 10 - 15cm from the center, as much polarization as c.a. 73% can be achieved. When it is located near the center or the outer boundary of the polarizer area, the polarization obtained is not much higher than one-pass polarization.
Fig. 4. Schematical design of a spherical-shaped reactor containing one layer of polarized $^3$He gas ($x$ designates the distance between the center and $^3$He gas layer).

Fig. 5. Thermal neutron polarization obtained in the center of the polarizer area as a function of the location of $^3$He gas cell layer, $x$ (see Fig. 4).

4.3. Effect of the Distribution of Polarized $^3$He gas cells

It is shown that we could polarize thermal neutrons effectively by inserting $^3$He gas cell layer into a reactor. However the polarization obtained in the previous subsection does not seem to be sufficient.

When $^3$He gas is located in a small region as in Fig. 5, neutron flux at and near the region is reduced and the effective polarizing ability of $^3$He would be weakened. It is, therefore, expected that we can achieve much higher polarization when $^3$He gas cells are homogeneously distributed over the polarizer area. According to this expectation, we calculated the thermal neutron flux and polarization in a reactor as shown in Fig. 6. In this figure, $^3$He polarizer is divided into five layers each with thickness of 0.2cm. The total thickness of $^3$He is 1cm, the same as in Fig. 4.

Figs. 7 and 8 show the results. Fig. 7 indicates that thermal neutron polarization is as much as c.a. $94\%$ in the center, which is surprisingly high compared with one-pass polarization$(55.7\%)$, and confirms the prediction. These figures also indicate that the polarization is higher and the flux is lower at positions where $^3$He gas layers are located.
5. CONCLUSION

Highly polarized thermal neutron field can be obtained in principle when polarized $^3$He filters are located in a nuclear reactor. The polarization of thermal neutrons in the center of the polarizer area would be much higher than obtained when the neutron beam passes through the cells just once outside a reactor or an accelerator.

Moreover, thermal neutrons could be polarized more effectively by homogeneously distributed cells over the polarizer area, instead of locating them in a small region which causes the neutron self-shielding effect in the $^3$He gas cells. More improvements can be expected by the optimum spatial configuration of polarized $^3$He filters. Although the system used and the calculation carried out in the present study are very simple, the essence of our results would remain unchanged in more complicated reactor design and calculation.
Fig. 8. Thermal neutron flux in each spin state in the polarizer area as a function of the distance from the center when $^3$He gas cells are arranged as shown in Fig. 6. Solid and dashed lines correspond to neutrons in parallel and antiparallel spin states to the $^3$He polarization respectively. The arrows designate positions of five $^3$He gas cell layers.

Many problems, however, must be overcome in order to realize our concept. It is necessary to increase the accuracy of the calculations presented here. To make it possible, spin-dependent differential cross sections of neutrons of middle and high energy region for many materials are required. In addition, a high amount of laser power is required to polarize a sufficient number of $^3$He nuclei by spin exchange with optically pumped Rb atoms and it costs much. The development of simpler neutron spin filters as well as high power laser is desired. We believe that our concept is challenging and interesting despite these difficulties.

ACKNOWLEDGMENT

The authors would like to thank Y. Masuda of KEK for his helpful advises.

REFERENCES

1) see e.g., Y. Masuda, et al.: KEK Preprint 91-127, October(1991); to be published in Hyperfine Interactions.
3) private communication with Y. Masuda of KEK.
THERMO-LUMINO DETECTOR FOR A NEUTRON DIFFRACTATION

Masanori HIDA, Tsuneo MORISAKI, and Masakazu NISHI

Department of Physics, Kyushu University
Hakozaki, Higashiku, Fukuoka 812, Japan

Institute for Solid State Physics, University of Tokyo
Roppongi, Minato, Tokyo 106, Japan

ABSTRACT

We have been developing a new detector system for the neutron diffraction camera. The system is mainly based on a thermoluminescence effect. The thermoluminescence sheet is made of a thermal luminosity being fine powders of rare earth doped BaSO_4 phosphors, and a (n-α) reactor of 187_BaO_a compound. The ionising radiations of the α-particles excite the thermal luminosity, and its stored energy is emitted as the thermoluminescence of about 370 nm on heating up to about 250°C. Two-dimensional thermoluminescences are detected and amplified by an imaging intensifier and converted by a CCD camera to electrical signals (vision image data). A computerized vision system can handle the signals and analyze the vision image. After gathering the thermoluminescences, the thermo-lumino sheets can be cyclically used by an annealer which eliminates the recorded image data.

INTRODUCTION

Some kinds of position-sensitive proportional detectors have been developed for the neutron diffraction to observe two-dimensional reciprocal space at a same time. It is also well known that a film method is often convenient. Usually, a LiF + ZnS(Ag) sheet is used as a scintillator of neutron beams and its sheets sandwich a X-ray film to be a photon-detector, for the neutron diffraction camera. At the present work, we applied the thermal luminoity of BaSO_4:Er, Cl compound to the neutron detector. The production of the thermoluminescence is schematically drawn in Fig.1. The figure represents a simple energy band configuration in a real crystal which includes some kinds of intrinsic defects. After ionizing radiation is absorbed in the crystal, the electrons are transformed from a valence band to a conduction band and the positive holes are
Fig. 1 Simple energy band model for a thermoluminescence

simultaneously produced in the valence band. Thus, the
electrons are freely to move through the crystal. However, it
is probable that such free electrons may be trapped at the
defects. That is, the electrons occupy trapping levels, as
shown in Fig. 1. The trapped electrons will remain in their
traps provided that they do not acquire sufficient energy to
escape. If the temperature of the crystal is raised, the
trapped electron may be released from the trapping levels and
have an opportunity to recombine with the holes. The excess
thermal energy is radiated from the crystal as visible or
ultraviolet photons, that is, thermoluminescence. Thus, we
tried to relate a brightness of the thermoluminescence to a
neutron absorption efficiency quantitatively.

EXPERIMENTS

Although various materials have been studied as a bright
thermoluminescence phosphors, we used the rare earth compound
doped in BaSO₄ phosphor; BaSO₄ : Er, Cl. The poly-crystalline
phosphor emits the thermoluminescence of about 370 nm. on
heating up to about 250 °C. Fig. 2 shows a schematic grow curve
of the present phosphor, taken with heat rate of about
10 °C/sec. The area and peak height of the grow peak depend on the
number of associated electron traps. Thus, the grow peak is
directly proportional to the stored energy in the phosphor,
if there are sufficient sites of the trapping level to the
ionizing radiations. We found that the present thermo-lumino
sheet had an excellent linearity to the ionising radiation and
its dynamic range was more than 6 places. In order to detect
the neutrons diffracted by the specimen, we utilized the (n-α)
reaction of 10 B in the 10 B₂O₃ compound. Thus, α-particles may
behave as ionising radiation of BaSO₄ phosphors, as shown in
Fig. 1. Experimentally, we succeeded to increase the neutron
absorption efficiency by a thinner coating of 10 B₂O₃ compounds
on each surface of poly-crystalline BaSO₄ phosphors of about 30
μm in diameter. The thermo-lumino sheet of 10 B₂O₃-BaSO₄ : Er,
Cl had a thickness of about 200 μm and flexible. We also found

- 998 -
Fig. 2 Glow curve of BaSO$_4$:Er,Cl

Fig. 3 Peak profiles of (111) Ge

Fig. 4 Curve of the intensity versus exposure time

that the thermo-lumino sheet was quite stable against lighting, drift of temperature and humidity, and fading. Thus, we can keep the stored energy in the trapping level, that is, the neutron diffraction images for a long time, if necessary. On heating, two-dimensional thermoluminescences emitted from the thermo-lumino sheet were detected and amplified by the imaging intensifier and converted to the electrical signals by the CCD camera. Furthermore, we could cyclically use the same sheet by the thermal treatment, since the trapping levels of electrons might be emptied by using the annealer.

We carried out the following experiments of the neutron diffraction to estimate some characters of the present thermo-lumino sheets. They were done at a cold neutron station, C1-1 of JRR-3 in Japan. Fig. 3 shows an areview of the vision image computerized on the displacement. The diffraction peaks were (111) reflections of Ge monochromator. The data were taken with different exposure time from 2 sec to 20 sec, as shifting the incident position of the diffracted neutrons on the thermo-lumino sheet of which size was 100x100 mm$^2$. The size of the incident beam was about 5 mm in diameter. Since the vision image quantitatively gave the integrated intensity of the
Fig. 5 Vision image of a specimen holder filled with powders reflections, we drew a curve of the intensity versus exposure time as shown in Fig. 4. We found that the linearity was satisfied to the neutron flux density except the data taken with the exposure time of 18 sec and 20 sec. The inconsistency depends on a selection of the sensitivity-range of the imaging intensifier. Thus, if we will set the lower sensitivity, we can gain the good linearity to the higher neutron flux.

On the other hand, the thermo-lumino sheet is often convenient to observe a setting condition of the specimen to the incident neutron beams. Figs. 5-(a) and (b) show the areaview and plane view of the vision image which represents the position of a cylindrical Al-holder filled with the powder specimen. The data were taken with the exposure time of 60 sec. The intensity valley in the figures was made by the neutron absorption of the specimen. Fig. 6 shows the peak profiles partially integrated along a vertical direction, as shown in Fig. 5-(b).

Fig. 6 Peak profiles partially integrated in Fig. 5-(b)
Fig. 7 Vision images of some reflections taken in a KCaF$_3$ crystal

Therefore, it is easy to set the accurate position of the specimen to the incident neutron beams as observing the vision image of the thermo-lumino sheet. It is also probable that we will be able to study a spatial distribution of inner defects in the material as like those of a neutron topography, though we need to further improve a spatial resolution and a ratio of signals to noises.

For other example of the application, we carried out measurements of an intensity-map of some reflections in order to study a structural phase transition of pseudo-perovskite KCaF$_3$. Figs. 7-(a) and (b) show the areaview and plane view of the reflections taken at room temperature with the oscillation range of 15 degrees and the exposure time of 9 hours. The thermo-lumino sheet was set in a film cassette of a simple neutron diffraction camera. In the figures, we observed a (2,0,0) fundamental reflection, (3/2,1/2,±1/2) superlattice reflections and a (3/2,1/2,0) superlattice reflection having a weak intensity. In addition to these reflections, we also observed background-reflections of Al-powders. Aluminium materials had been used in a shield of a specimen room at the

Fig. 8 Superlattice reflections of KCaF$_3$
present experiment. We could reduce the background by setting an oscillated radial slit having many $\text{Gd}_2\text{O}_3$ sheets around the specimen room. Therefore, it is useful to simultaneously observe two-dimensional view of the reciprocal lattice space to study any crystallographic and/or magnetic structural modifications.

Figs. 8-(a), (b) and (c) show the areaviews of the fundamental and superlattice reflections reduced the background reflections of Al-powder. The oscillation range and the exposure time were (2°, 5 min), (3°, 25 min) and (5°, 45 min) in Figs. 8-(a), (b) and (c), respectively. Fine structures of these reflections may be mainly related to multi-domains which were produced by the structural phase transition occurring at higher temperature. To study the phase transition, we carried out measurements of the temperature-dependence of the integrated intensity of the $(3/2, 1/2, 1/2)$ superlattice reflection shown in Fig. 8-(b). Fig. 9 represents a curve of the

![Graph](image)

Fig. 9 Temperature dependence of the integrated intensity of $\text{KCaF}_3$ integrated intensity versus temperature. Each data was taken with the oscillation range of 3 degrees and the exposure time of 10 min. We confirmed that there was the structural phase transition at about 290°C.
DISCUSSION

At the present investigations, we found that the thermo-lumino detector was one of the convenient tools for the neutron diffraction. Especially, the repeating utilization and flexibility of the thermo-lumino sheet may produce a new type of neutron diffraction camera. Since the sheet is quite stable to the condition of atmosphere and to the external stress, we can quantitatively measure the stored energy, being directly proportional to the absorbed neutron flux, as the thermoluminescence at any time. Two-dimensional vision image of the reciprocal lattice space may clearly indicate a crystallographic and/or magnetic structural property related to modulated diffuse scatterings, incommensurate superlattice reflections or satellite reflections. Although we need to further improve the neutron absorption efficiency and the ratio of signal and noise of the thermo-lumino detector, its application will be extended to the various neutron and γ-ray diffractions and may achieve an important front work to ordinary proportional counters.
DEVELOPMENT OF NEUTRON OPTICAL DEVICES IN JRR-3M

Kazuhiko SOYAMA, Masatoshi SUZUKI, Yuji KAWABATA*, Hiroki ICHIKAWA and Tsuneo KODAIRA

Department of Research Reactor
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki, 319-11 Japan

*Research Reactor Institute
Kyoto university
Kumatori-cho, Sennan-gun, Osaka, 590-04 Japan

ABSTRACT

Two thermal neutron guide tubes and three cold neutron guide tubes have been installed at the JRR-3M with a cold neutron source. Development of the neutron optical devices has progressed. In this paper, we describe the characteristics of the natural nickel guide tubes at the JRR-3M and recent developments of the neutron optical devices such as supermirror and neutron bender.

INTRODUCTION

According to the successful work at ILL from early 1970s, the uses of cold neutron beam guided from the cold neutron source have enlarged neutron research field. Nowadays neutron beam is one of the most important tools to study physics, chemistry, earth, material, and biology, as well as X-rays. Recently middle class research reactors, such as the JRR-3M (renovated 1990) at Japan Atomic Energy Research Institute, the NBSR (renovated 1990) at National Institute of Standards and Technology and the BER-II (renovated 1991) at Hahn-Meitner-Institut have been upgraded to have a cold source and neutron guide tubes, and ultra high flux reactor, ANS (Advanced Neutron Source) has been planned to achieve criticality in 2002 in order to meet the increasing demands on neutron beam research.

Abreast of the development of neutron source, techniques for tailoring neutron beams such as transporting, monochromating, focussing and polarizing, have been developed to advance neutron instrumentations at each research centers. Development of these neutron optical devices meets the research demands and furthermore will open up new research field.

In this paper, we describe the characteristics of the neutron guide tubes at the JRR-3M and recent development of the neutron optical devices such as a supermirror neutron guide tube and a neutron bender.

NEUTRON GUIDE TUBES AT THE JRR-3M

The upgraded JRR-3 (Japan Research Reactor No.3) is a pool type, light water-moderated and cooled reactor with heavy water reflector (20MW). The JRR-3M is normally operated 9 cycles a year, each cycle consists of 26 days operation. Maximum thermal neutron flux in the heavy water reflector is 2.5 x 10¹⁴ n/cm²/sec. Neutron guide tubes and a cold neutron source have been installed. General layout of the neutron guide tubes and neutron facilities at the JRR-3M are shown in Fig.1. A beam hall, which is 30m wide and 50m long, gives a spacious experimental area. Two thermal neutron guide tubes (T1 and T2) are about

— 1004 —
60m long with 2Å characteristic wavelength. Three cold neutron guide tubes (C1, C2 and C3) are about 31-51m long. The characteristic wavelengths of C1 and C2 are 4Å and that of C3 is 6Å. The total length of all the guide tubes is 232 m, and there are 17 neutron ports for neutron beam experiments in the beam hall. The main parameters of the guide tubes are shown in Table 1. The neutron mirrors are made of nickel sputtered borosilicate glasses. Nickel is natural and nickel layer is about 2000Å thick. These guide tubes consist of short straight units which are 85cm long. The length of these units is short enough to make good polygonal approximation and it is also long enough to lessen for a number of conjunctions. They are curved in the guide tunnel and shielding room and straight in the beam hall. The beam cross-section of the thermal guide tube is 2cm x 20cm, and that of the cold guide tube is 2cm x 12cm. Neutron fluxes at the exit of thermal neutron guide tubes, T1 and T2, (characteristic wavelength 2Å) were 1.2 x 10^8 n/cm²/sec at a reactor power of 20MW. Those at the end of the cold guide tubes were 2 x 10^8 n/cm²/sec for C1 and C2 (characteristic wavelength 4Å), and 1.4 x 10^8 n/cm²/sec for C3 (characteristic wavelength 6Å).

![Diagram](image)

Fig.1 General layout of the neutron guide tubes at the JRR-3M

<table>
<thead>
<tr>
<th>Guide tube</th>
<th>Characteristic wavelength (Å)</th>
<th>Beam cross-section (mm²)</th>
<th>Radius of curvature (m)</th>
<th>Length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>2</td>
<td>20 x 200</td>
<td>3373.4</td>
<td>59.91</td>
</tr>
<tr>
<td>T2</td>
<td>2</td>
<td>20 x 200</td>
<td>3373.4</td>
<td>58.98</td>
</tr>
<tr>
<td>C1</td>
<td>4</td>
<td>20 x 120</td>
<td>834.3</td>
<td>30.75</td>
</tr>
<tr>
<td>C2</td>
<td>4</td>
<td>20 x 120</td>
<td>834.3</td>
<td>51.08</td>
</tr>
<tr>
<td>C3</td>
<td>6</td>
<td>20 x 120</td>
<td>370.8</td>
<td>31.38</td>
</tr>
</tbody>
</table>

DEVELOPMENT OF SUPERMIRROR

The neutron mirror of the JRR-3M guide tube is based on the total reflection phenomenon. The critical reflection angle of natural nickel is 1.7 mrad/Å and that of 58Ni is 2.0 mrad/Å. Supermirrors which is based on the bragg reflection and total reflection, can extend the critical reflection angle up to 2–3 times that of natural nickel. So supermirror guide tube can enhance the angular divergence and intensity of transmitted neutron beam at the exit of the neutron guide tube.

Ni/Ti supermirror with high reflectivity has been developed at JAERI. The dependence of surface roughness of the substrate on neutron reflectivity has been investigated in order to
increase neutron reflectivity. The reflectivity measurements of the supermirrors deposited on float glass substrates with different surface roughness, were performed at the JRR-3M. The surface roughness of the polished substrate is 5.1Å rms and 30.9Å peak to valley, that of the non-polished substrate is 7.6Å rms and 45.4Å peak to valley, and that of the rough polished substrate is 10.0Å rms and 59.8Å peak to valley, which were measured by the Zygo Heterodyne Profiler (ZYGO-5500). Ni/Ti supermirrors with 125 layers (28Ni) were deposited on the float glass substrates (300 x 100 x 10mm) by the electron beam evaporation system. The neutron reflectivity measurements were carried out by the time of flight method at the thermal neutron guide tube (TI-4) of JRR-3M. They were performed at a grazing angle of about 1x10^-2 rad with an angular resolution Δθ/θ of the order of 1x10^-3 rad and with neutrons of wavelength over a spectral range of λ from 1Å to 8Å. Fig.2 shows the measured reflectivities of supermirrors with 125 layers. The critical wavelength of these supermirrors is 300Å, which is as half as that of natural nickel. The measured reflectivities increase rapidly at the critical wavelength. It becomes higher with increasing neutron wavelength up to unity for wavelength longer than the critical wavelength of natural nickel. The comparison among these mirrors shows that neutron reflectivity strongly depends on the surface roughness. The reflectivity of supermirror whose surface roughness is 5.1Å rms is greater than 90% at the critical wavelength.

The morphology and multilayer structure were observed by transmission electron microscope (TEM) method. Fig.3 shows the TEM image of the Ni-Ti multilayer consisting of 20 bilayers with d=150Å near the silicon substrate. The dark layers correspond to nickel layers, and the bright layers correspond to titanium layers. It is seen the Ni/Ti multilayer has smooth and uniform interface. Fig.4 shows the TEM image for the same sample which was observed in the upper bilayers. The layer is beginning to undulate with increasing the number of layers. The d-spacing is maintained, but the interface has big undulation in layer thickness. The crystallization is observed in the nickel layers, which damage the smooth interfaces. The titanium layers show amorphous structure.
SUPERMIRROR BENDER

Neutron bender can branch off a white neutron beam from a main beam line, and create a new beam port for various beam experiments. A neutron bender using supermirrors can make radius of curvature to be smaller and makes it much easier to separate a neutron beam. General scheme of a supermirror neutron bender is shown in Figure 5. This bender has eleven channels which are divided by float glass plates. Both sides of glass plate are coated by Ni-Tisupermirror with $2\theta_{Ni}$. Each channel is 2.0mm in width and glass plate is 0.5mm in thickness. Neutron beam size of this bender is 150mm in height by 27mm in width. Total length of this bender is 2m. The characteristic wavelength at the exit of this bender is 8Å. Transmission rate was evaluated using the NEUGT code\(^{10}\) assuming a supermirror reflectivity to be 90%. This code was developed to calculate neutron transmission for the design assessment of neutron guide tubes at the JRR-3.\(^{11}\) The supermirrors with 254 layers have been already coated on the both side of the glass plate which is 0.5mm thickness. This neutron bender is planed to be set at the end of cold neutron guide tube (C2-3) whose characteristic wavelength is 4Å.

![Diagram](image)

Fig. 5 General scheme of a supermirror bender

CONCLUSIONS

We have developed the natural nickel guide tubes which were already installed at the JRR-3M, and we have advanced the neutron optical devices such as supermirror and its applications like a neutron bender in order to meet increasing demands and will open up new research field. Ni-Ti supermirror with high reflectivity (>90%) has been developed by using electron beam evaporation system, and a supermirror neutron guide tube and a supermirror bender are under development.

ACKNOWLEDGEMENTS

The authors would like to thank Drs. T. Ebisawa, S. Tasaki for useful discussion about making supermirror. The supermirror were fabricated by Nikon corporation.

REFERENCES


NEUTRON MEASUREMENTS AS FUSION PLASMA DIAGNOSTICS

Takeo. Nishitani and *Magnus. Hoek

Department of Fusion Plasma Research
Naka Fusion Research Establishment, JAERI
Naka-machi, Naka-gun, Ibaraki-ken 311-01, Japan

*STA Fellow

ABSTRACT

Neutron measurements play important roles as the diagnostics of many aspects of the plasma in large tokamak devices such as JT-60U and JET. In the d-d discharges of JT-60U, the most important application of the neutron measurement is the investigation of the fusion performance using fission chambers. The ion velocity distribution function, and the triton slowing down are investigated by the neutron spectrometer and the 14 MeV neutron detector, respectively. TANSY is a combined proton-recoil and neutron time-of-flight spectrometer for 14 MeV neutrons to be used during the d-t phase at JET. The detection principle is based on the measurements of the flight time of a scattered initial neutron and the energy of a corresponding recoil proton. The scattering medium is a polyethylene foil. The resolution and efficiency, using a thin foil (0.95 mg/cm²), is 155 keV and 1.4 × 10⁴⁻⁵ cm², respectively.

INTRODUCTION

The controlled nuclear fusion is regarded as the ultimate energy source in future. The tokamak is the leading device in the nuclear fusion research. Fusion plasma is so complicated that many measurement methods are needed to diagnose the plasma property such as density and temperature. In the deuterium plasma, the following fusion reactions take place with nearly equal probability:

\[ d + d \rightarrow n (2.45 \text{ MeV}) + ^3\text{He} (0.82 \text{ MeV}) \]
\[ d + d \rightarrow p (3.02 \text{ MeV}) + ^3\text{He} (1.01 \text{ MeV}) \]

Those fusion reactivities are strong functions of the ion temperature in the thermal plasma. The neutron measurement was regarded as the ion temperature diagnostics in the first stage of the fusion study, because the neutron energy spectrum from the thermal plasma has a Doppler broadening (FWHM) of 82.5\sqrt{T_i} for d-d reactions, where T_i is the ion temperature. In the most of the medium and large tokamaks such as JET in EC, JT-60U in Japan, TFTR and DIII-D in USA, operating routinely with deuterium plasmas, additional heating as neutral beam injection (NBI) and/or radio frequency (RF) heating is employed to obtain the break-even plasma. In those plasmas, the neutron spectroscopy is no longer useful as the ion temperature diagnostics, where the width of the neutron spectrum dose not depend on T_i only. However, neutron measurements becomes more important as the diagnostics of many aspect of the plasma.

JT-60U¹) is one of the large tokamaks to study of the reactor-grade plasmas near fusion power break-even conditions. The major parameters of JT-60U are the plasma current of 6 MA, the major radius of 3.4 m, the minor radius of 1.1 m the and the plasma volume of 100 m³. This
paper describes the present status of the neutron diagnostics of the d-d plasma on JT-60U. JET\(^2\) has a plan of the d-t operation in 1996. The new neutron spectrometer, TANSY, has been developed for the d-t experiments employing the time-of-flight technique.

**NEUTRON YIELD MEASUREMENTS ON JT-60U**

The most important application of the neutron measurement in the tokamak is the evaluation of the fusion power, which is derived directly from the total neutron yield. The time-resolved neutron yield is measured with \(^{235}\)U and \(^{238}\)U fission chambers in JT-60U\(^3\). A fission chamber, which is an ionization chamber whose wall is coated by fissile material such as \(^{235}\)U and \(^{238}\)U, is suitable for the neutron source strength measurements for d-d plasmas. Energy released by fission is so large, 150 - 200 MeV, that it is easy to reject the effect of \(\gamma\)-rays whose energy is not more than 20 MeV in the d-d operational tokamaks. Large charge generated by fission reactions enable us to use it in current mode, so a wide range of the neutron flux, typically 9 or 10 decades, can be measured.

The \(^{235}\)U detector is used in the low and medium neutron yield discharges and the \(^{238}\)U detector is used in the high neutron yield discharges such as high-power NB heating experiments. Those detectors were placed on the torus midplane, just outside the toroidal field coils, at three different toroidal bays. The detectors are all long cylinders in geometry. The \(^{235}\)U detector is surrounded by a 50 mm thick polyethylene moderator, and 1 mm thick cadmium thermal neutron shield. This detector's neutron sensitivity is estimated to be almost constant in the energy range of 0.55 eV to 2.5 MeV. The \(^{238}\)U detector is surrounded by a 50 mm thick lead gamma shield only. The detectors were oriented vertically and placed just beyond the outer diameter of the toroidal field coils to reduce the effects of the magnetic fields. Being in line with midplane ports, the detectors had a minimum of shielding between themselves and the plasma neutrons.

We use \(^{235}\)U and \(^{238}\)U fission chambers in both pulse counting mode and Campbell (MSV) mode. The former is suitable for low count rates less than \(10^6\) cps and the latter is for high count rates more than \(10^5\) cps. By combination of both modes, wide dynamic range of 10\(^10\) was obtained. The temporal resolution of 2 ms has been completed by the combination of three linear amplifiers with different gain in the Campbell mode.

The absolute calibration of the relation between the neutron source strength in the whole plasma and the output of neutron monitor is the most important problem in the measurements of the neutron yield. The calibration is rather difficult because the neutron source is distributed in the plasma which is surrounded with many complicated structures such as first wall, vacuum vessel poloidal and toroidal coils. The absolute detection efficiencies of the neutron detectors were measured for 92 locations of the neutron point source in toroidal scans at two different major radii in the JT-60U vacuum vessel. The total detection efficiency for the torus neutron source was obtained by the averaging the point efficiencies over the whole toroidal angle. The uncertainty of the neutron yield is evaluated to be \(\pm 11\%\).

Figure 1 shows the typical waveforms of the total neutron yield in the Neutral Beam (NB) heated discharge. Typical discharge duration is 15 s in JT-60U. In this discharge, 23 MW of NB was injected from 4 s to 6 s. We obtained the maximum neutron yield of \(2.8 \times 10^{16}\) n/s at 4.85 s. The increase of the neutron yield is terminated by the \(\beta_p\) collapse which is one of the MHD instabilities. The tokamak plasma analysis shows that about half of the neutron yield is contributed by the thermal fusion reactions, 40 % is the beam-thermal reactions and the other is the beam-beam reactions. The fusion gain \(Q_{\text{HH}}\) defined by (output power/input power) is \(1.5 \times 10^{-3}\) in this discharge. The performance of equivalent d-t discharge was simulated by assuming D\(^0\) beam injecting and 50/50 d/t target plasma using same temperatures and electron density profile, beam power, and other parameters as a comparable d-d discharge. By the analysis, the
equivalent d-t fusion gain $Q_{dt}$ was estimated to be 0.25 for this discharge, which is quarter of the breakeven condition.

![Graph showing NB Power vs Time and Neutron Yield vs Time]

**Fig. 1.** Typical waveforms of the total neutron yield in the Neutral Beam heated discharge

**NEUTRON SPECTROSCOPY ON JT-60U**

Neutron energy spectrum produced from d-d and/or d-t burning plasmas reflects several properties of the ion velocity distribution function. A $^3$He gas ionization chamber ($^3$He I.C.) was proved as a successful tool for d-d plasma neutron diagnostics in the large tokamak machines such as JET and TFTR. In JT-60U, the same type of $^3$He I.C. has been installed and applied to d-d plasma neutron spectrometry.

The $^3$He I.C. used in JT-60U is the same type fast neutron spectrometer as already experienced in many other tokamaks, which is called FNS-1 on the market. For 2.45MeV d-d neutrons, the energy resolution of this detector can be 50 keV FWHM. An adequate unfolding code with the detector response functions is needed to obtain neutron spectrum from the measured pulse height data. In this study, the response functions of the $^3$He I.C. in the energy range between 0.1 and 5.0 MeV were prepared through Monte Carlo calculation. These calculational results were adjusted to agree with the measured response data for several kinds of monoenergetic neutron sources. The spectrum unfolding code was based on the maximum likelihood and the maximum entropy method. On the other hand, the FPS (Fusion Product energy Spectrum) code was adopted to interpret the measured neutron spectra. This Monte Carlo code calculates the energy spectrum of a fusion product for given energy distribution functions, such as Maxwellian distribution, solutions of Fokker-Planck equation etc., of the primary reacting ions in a tokamak plasma. The reasonable ion energy distribution can be estimated by searching the best agreement between experimental and theoretical neutron spectra.

The $^3$He I.C. was placed at about 15 m distance under the center of the vacuum vessel. Through a collimator, the view area is subtended around 10 cm in diameter. The performance of the present neutron spectrometry system were checked for some ohmically and beam heated deuterium plasmas, of which average neutron emission rates were limited to suppress the pile-up effect in pulse height measurement, about $5 \times 10^{12}$ n/s in ohmic heating only and $4 \times 10^{14}$ n/s in 4MW NB heating, respectively.

Figure 2 shows the typical neutron spectrum from the NB heated deuterium plasma. Deuterium NB of 90 keV are injected into the plasma with the injection angle of 75 deg. against the magnetic axis, while, to this axis, the viewing angle of the neutron spectrometer is 90 deg. Due to anisotropy of the beam ion velocity distribution, dual peaks of the neutron spectrum are observed in the measured pulse height data. Assuming the background ion temperature of 4.0 keV combined with the analytical solution of Fokker-Planck eq. in the FPS code, good
agreement is found between the calculated and the unfolded neutron spectra as shown in Fig. 2(b).

![Neutron spectrum](image)

**Fig. 2.** Neutron spectrum in NB heated d-d plasma: (a) Measured pulse height spectrum and (b) Unfolded neutron spectrum.

**TRITON BURNUP STUDY IN JT-60U**

The behavior of 1 MeV tritons produced in the d(p,t) reaction is important to predict the properties of d-t produced 3.5 MeV alphas because 1 MeV tritons and 3.5 MeV alphas have similar kinematic properties such as Larmor radius and precession frequency. The confinement and slowing down of the fast tritons were investigated by measuring the ratio of the 14 MeV and the 2.5 MeV neutron production rates. Tritons of 1.0 MeV are produced in the d(p,t) reaction at the same rate as the 2.5 MeV neutrons from the d(d, n)\(^3\)He reaction. The majority of these tritons will remain confined in the plasma and slow down and a small fraction will undergo the fusion reaction t(d, n)\(^4\)He, in which 14 MeV neutrons are produced. Time resolved triton burnup measurements were carried out by a 14 MeV neutron detector and they are compared with classical slowing down calculations.

The time-resolved 14 MeV emission rate was measured with the silicon surface barrier diode (SBD). The 14 MeV neutrons entering a silicon diode may undergo the following nuclear reactions: \(^{28}\)Si (n, p) \(^{28}\)Al and \(^{28}\)Si (n, α) \(^{25}\)Mg, which have effective thresholds of about 7 MeV. Thus, the above reactions do not occur for the far more abundant 2.5 MeV neutrons. The SBD is mounted in the 20 cm-thick lead cylinder to shield gamma-rays from neutron capture events in the surrounding structure. The detector was installed just outside the JT-60U vacuum vessel on the midplane as close to the plasma as possible. A thin disk with a \(^{241}\)Am alpha particle source is mounted in front of the SBD to make an energy calibration of the detector possible using 5.486 MeV alphas. The 14 MeV neutron yield integrated over several weeks was measured by the activation foils using the \(^{93}\)Nb(n, 2n)\(^{92}\)mNb reaction, which has a threshold energy of 9 MeV, a flat response function around 14 MeV, and a large cross-section. Because a pneumatic foil transfer system was not available at that time, the foil was irradiated in the re-entry port only 16 cm outside the typical plasma surface. The absolute error in the 14 MeV emission rate was estimated to be ±20% including the calibration uncertainty of ±20%.

The time-dependent 14 MeV neutron emissivity was simulated by a simple classical slowing down model. The plasma was divided into 11 annular shells in the calculation. In each shell, the tritons were divided into 400 groups according to their birth time, with 10 ms time bins. The number of tritons in a group is proportional to the 2.5 MeV neutron emissivity at the
birth time of the tritons. Tritons were allowed to slow down in each shell according to the classical energy loss theory.

Figure 3 shows the temporal evolution of the 2.5 MeV and 14 MeV neutron emission rates in a plasma with NBI heating of 18.7 MW. The peak of 14 MeV neutron emission was delayed due to the slowing down of the tritons from 1 MeV to the peak of d(t,n)α cross-section at 170 keV of the triton energy. The delay is very sensitive to the slowing down process of the triton, but not to the confinement time. The calculated 14 MeV emission rate is also shown in Fig. 1. There is good agreement between the measured and the calculated temporal evolution of the 14 MeV emission rate, indicating that the slowing down process of the 1 MeV tritons is classical.

![Graph showing neutron emission rate vs time]

**Fig. 3.** Comparison of predicted and measured 14 MeV neutron emission rate for the NB heated d-d plasma.

### THE TANSY SPECTROMETER

The TANSY spectrometer(6,7,8) is a combined proton-recoil and neutron time-of-flight spectrometer designed for measurements of neutrons in the energy range 10-18 MeV at JET. The spectrometer has been constructed and built by the department of Reactor Physics at Chalmers University of Technology in Sweden and will be installed at JET before the D-T phase starts. The instrument will be positioned ca 20 m above the torus in a roof lab and the neutrons to be analyzed, enter the spectrometer through a collimator and scatter in a polyethylene foil, aligned with the neutron beam. In the foil, scattering can take place against hydrogen nuclei which gives rise to a recoiled proton and a scattered neutron. The recoil proton is detected by one of six proton detectors, three on each side of the foil, where the energy and time of the proton is measured with high accuracy. For the scattered neutrons, the most accurate method to measure the energy is by a time-of-flight method, where the time-difference between the detection of the proton and the neutron is measured. The scattered neutron is detected by one of 32 neutron detectors grouped into two detector banks with 16 detectors on each side of the foil. Thus, the energy of the source neutron can be obtained as the sum of the energies of the recoil proton and the scattered neutron.

The principle of TANSY is shown in Fig. 4. The figure shows the collimator, the scattering foil, the proton detectors and the neutron detector banks. The neutron detectors in each bank are split into an upper and a lower row. The surfaces of the neutron detectors are positioned on the surface of a sphere with radius 100 cm and its centre coinciding with the centre of the foil.
Fig. 4. The principle of the TANSY spectrometer. Source neutrons enter through the collimator (1). A fraction of the neutrons scatter against hydrogen nuclei in a polyethylene foil (2). The recoil protons are detected in one of the six proton detectors (three on each side of the foil) (3) while the corresponding scattered neutron is detected by one of the 32 neutron detectors (16 on each side of the foil) (4). From ref. 8.

The foil is strained between two vertical rods on a plate placed on the bottom of a vacuum vessel containing the proton detectors (silicon diodes). For a detected proton, the time, which is used as a start signal for a time-digital-converter (TDC), and the amplitude of the signal are measured. The stop (neutron) detectors are fast plastic scintillators connected to a photomultiplier (PM) tube. Each neutron detector is surrounded by a 2 mm thick magnetic shield of µ-metal.

The TANSY spectrometer has been tested at the laboratory, using 14 MeV neutrons from a neutron generator. The instrument may be used utilizing several different thicknesses of the foil in order to enable a choice between different efficiencies and corresponding resolutions. Analytical calculations of the efficiency, and measured resolutions, have been confirmed with Monte Carlo simulations9. The measured and simulated response functions, for two different thicknesses of the foil, are shown in figs 5 and 6.

Fig. 5. Comparison of the response functions obtained from experiment and Monte Carlo calculations. The experimental distribution has been corrected for background and is also normalized. The units on the y-axis refer to the simulated response function. The simulated source neutrons are Gaussian disturbed with an FWHM of 178 keV, which is the estimated energy spread of the neutron generator. The foil thickness, which is the thinnest used, is 0.95 mg/cm² and the FWHM of the response function is 230 keV. From ref. 9.
Fig. 6. Comparison of the response functions obtained from experiment and Monte Carlo calculations. The experimental distribution has been corrected for background and is also normalized. The units on the y-axis refer to the simulated response function. The simulated source neutrons are Gaussian disturbed with an FWHM of 178 keV, which is the estimated energy spread of the neutron generator. The foil thickness, which is the thickest used, is 16.0 mg/cm² and the FWHM of the response function is 2050 keV. From ref. 9.

The response functions obtained from Monte Carlo calculations will be used for the unfolding of measured neutron energy spectra at JET. The simulated response functions are therefore calculated with a monoenergetic initial neutron energy and a parallel neutron beam. The results from such assumptions result in better values of the resolution due to the absence of the energy spread from the neutron generator. Calculated values of the efficiency and resolution from different foil thicknesses are shown in table 1.

<table>
<thead>
<tr>
<th>Foil thickness [mg/cm²]</th>
<th>Efficiency [10⁻⁵ cm²]</th>
<th>FWHM [keV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>1.4</td>
<td>155</td>
</tr>
<tr>
<td>2.40</td>
<td>3.5</td>
<td>325</td>
</tr>
<tr>
<td>2.89</td>
<td>4.2</td>
<td>390</td>
</tr>
<tr>
<td>3.80</td>
<td>5.5</td>
<td>505</td>
</tr>
<tr>
<td>8.00</td>
<td>11.6</td>
<td>1050</td>
</tr>
<tr>
<td>16.0</td>
<td>23.2</td>
<td>ca 2050</td>
</tr>
</tbody>
</table>

In Fig. 7 the energy of monoenergetic source neutrons is scanned and the efficiency is calculated for a foil thickness of 0.95 mg/cm². Also shown is the efficiency if only singly scattered neutrons in the neutron detectors were encountered.
Fig. 7. The efficiency as a function of the source neutron energy for a foil thickness of 0.95 mg/cm². The efficiency from singly scattered neutrons should be compared with the analytical one. The curve for multiple scattering contains both singly and multiply scattered neutrons in the neutron detectors. It should be emphasized that the efficiency is calculated for 16 neutron and 3 proton detectors. From ref. 9.

The analytically calculated efficiency in Fig. 7 should be compared to the simulated efficiency for singly scattered neutrons. It can be seen that the efficiency increases with increasing neutron energy until a certain energy (ca 8 MeV) is reached. This energy depends on the chosen bias level of the neutron detectors. Source neutrons below 8 MeV give rise to scattered neutrons with an energy too low to exceed the bias level of the lower neutron detector row. Coincidences from the lower row are still present but only neutrons that enter the upper part of the surface of the detectors are registered. The efficiency above 8 MeV then decreases with increasing neutron energy due to the decreasing cross section of hydrogen which influences the scattering efficiency of both the scattering foil and the neutron detectors. It can be noticed that there is a discrepancy between the analytical and the simulated efficiency of ca 6%. This discrepancy relates to the analytical calculation which does not take into account such effects as the spatial neutron distribution in the neutron detectors.

Experiments in the laboratory have shown that it is possible to utilize the neutron-proton scattering process for a high precision neutron spectrometer. The obtainable efficiency of 10⁻⁻⁵ cm² is sufficient for neutron diagnostics during the D-T phase of a tokamak fusion reactor.

ACKNOWLEDGEMENTS

We would like to thank Dr. Y. Ikeda and Prof. T. Iguchi for their collaboration. One of us (M.H.) are indebted to the project leader of TANSY, Dr. G. Grosshög, for the permission to use the informations related to the TANSY spectrometer in this paper.

REFERENCES

7) G. Grosshög et al., CTH-RF-54, Chalmers University of Technology, Göteborg (1985).
CURRENT STATUS AND FUTURE OF UTILIZATION
IN RESEARCH REACTORS

YOSHIMI KOYAMA, YOSHIO HOSHI, DENJIRO NEMOTO,
HIDETAKE TAKAHASHI

Department of Research Reactor
Tokai Research Establishment, JAERI
Tokai-mura, Naka-gun, Ibaraki-ken, 319-11 Japan

ABSTRACT

In research reactors of Japan Atomic Energy Research Institute (JAERI), JRR-3 was upgraded (so called JRR-3M) with irradiation facilities and neutron beam experimental facilities. Particularly the new supply of cold neutrons brings to a great increase of fields of utilization in research reactors of JAERI. In JRR-4, it is planned to reduce the fuel enrichment and to renew several utilization facilities in several years. JRR-2 will be shut down also in several years because of its superannuation.

On the other hand most research reactors of other institutes in Japan have faced with their superannuation and the difficulties of refurbishment or upgrading as well as new construction because of the changes of environmental condition such as urbanization of their surroundings. The research reactors in JAERI will play more important role for research and development using neutrons in future than past and present (0). Therefore the investigation was made in order to catch the needs for utilization of research reactors. The results of this investigation show that there are many research institutes which hope to utilize research reactors in accordance with the increase of available fields such as research of high polymer, biology, industrial materials and components, and contribution to environmental investigation by using neutron scattering, neutron radiography and activation analysis. This means that the research reactor utilization will be able to contribute to general scientific fields as well as utilization for research and development of nuclear energy which have been popular as utilization of research reactors.

In this presentation, the current status of utilization of research reactors in JAERI and utilization fields of research reactors expected in future based on the investigation are described. It is also discussed what is important for the utilization to use effectively the research reactors in JAERI.

1. INTRODUCTION

Research reactors in JAERI have been widely used for research and industry works such as activation analysis, radiolotope production, irradiation tests on fuels and materials, neutron scattering, neutron radiography experiments, medical irradiation, reactor physics experiments, training for reactor engineers and so on since the first criticality of JRR-1 in 1957. For these utilizations research reactors are designed to produce high-density neutron
flux with relatively low thermal output. Research reactors in JAERI have been constructed as JRR-1 JRR-2 JRR-3 JRR-4 and JRR-3M. Utilization fields of research reactors have changed depending on the needs of research and development using reactors. The current status of utilization in the research reactors of JAERI is discussed in the chapter 3. It is important to know the available utilization fields and trend of research and development using neutrons for us to consider how to use research reactors in future. And it is also important to cultivate new utilization fields which have not been used in research reactors. For these purpose investigation was made.

2. INVESTIGATION OF UTILIZATION TREND

2.1 Method of investigation

Investigation was made for research institutes which have used research reactors and have not used those mainly by a questionnaire. The research institutes in Tukuba area were investigated as a representative of the institutes in JAPAN, which have not used research reactors.

2.2 Results of investigation

(1) For research institutes which have not used research reactors

Questionnaire with the explanation about basic theory and practical method of the utilization were sent to persons of 638 in research institutes and persons of 376 answered. Percentage answered was 58.9 %. In this investigation, 87 out of 131 research institutes which have not used research reactors are interesting in utilization of research reactors, and 30 research institutes intend to use research reactors. Table 1 shows these results in each utilization field.

Table 1 Interest of research institutes in each utilization field, which have not used research reactors.

<table>
<thead>
<tr>
<th>Utilization field</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation analysis</td>
<td>57</td>
<td>19</td>
</tr>
<tr>
<td>Neutron scattering experiment</td>
<td>50</td>
<td>11</td>
</tr>
<tr>
<td>Neutron radiography</td>
<td>48</td>
<td>8</td>
</tr>
</tbody>
</table>

(some numbers are overlapping)

A : Research institutes which are interested in each utilization field.
B : Research institutes which intend to use each utilization field.

However 57 out of 87 institutes which are interested in utilization of research reactors do not intend to use them because of following reasons shown in Table 2.

Table 2 Reasons why research institutes do not intend to use, although they are interested in utilization of research reactors.

<table>
<thead>
<tr>
<th>Reason</th>
<th>answers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utilization method is not known</td>
<td>24</td>
</tr>
<tr>
<td>Utilization procedure is not known</td>
<td>19</td>
</tr>
<tr>
<td>Budget is not estimated</td>
<td>16</td>
</tr>
<tr>
<td>Dislike to deal with radiation</td>
<td>3</td>
</tr>
<tr>
<td>Another facility can be used</td>
<td>28</td>
</tr>
<tr>
<td>Others</td>
<td>22</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>112</strong></td>
</tr>
</tbody>
</table>

(Some numbers are overlapping)
38.0% of institutes are not familiar with utilization method and procedure. This means that if utilization method or procedure are understood by researchers, they will use research reactors.

(2) For research institutes which have used research reactors
Utilization fields of the answered research institutes which have used research reactors are shown in Fig.1.

Fig.1 Utilization fields of research institutes which have used research reactors.

202 out of 245 institutes which have used research reactors intend to continue to use them in future. This means that 82 percent of users have a plan to use research reactors. Research reactors which users have a plan to use are shown in Fig.2.
The result of the investigation shows that new several fields of in-pile irradiation are expected, but the number of the irradiation might not be drastically increased.
Fig. 2 Research reactors which users are planning to use

Items which continue experiments or which are planning to begin new experiments in neutron activation analysis, neutron scattering experiment or neutron radiography are shown in Table 3.

Table 3 Number of items which continue experiments or which are planning to begin new experiments in each utilization field.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Items which continue experiments</td>
<td>283</td>
<td>84</td>
<td>21</td>
</tr>
<tr>
<td>Items which are planning to begin new experiments</td>
<td>167</td>
<td>138</td>
<td>23</td>
</tr>
<tr>
<td>Total</td>
<td>450</td>
<td>222</td>
<td>44</td>
</tr>
</tbody>
</table>

(Some numbers are overlapping)

A: neutron activation analysis, B: neutron scattering experiment, C: neutron radiography

Quite many users are interested in and intended to try to use new utilization fields such as activation analysis of extremely short life nuclide or prompt gamma ray activation analysis as shown in Table 4.
Table 4 New utilization fields which are intended to try to use by users.

<table>
<thead>
<tr>
<th>New utilization field</th>
<th>Answers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation analysis for very short life nuclide</td>
<td>37</td>
</tr>
<tr>
<td>Prompt gamma ray analysis</td>
<td>29</td>
</tr>
<tr>
<td>Nuclide chemistry</td>
<td></td>
</tr>
<tr>
<td>Nuclear reaction</td>
<td>13</td>
</tr>
<tr>
<td>Hot atom chemistry</td>
<td>8</td>
</tr>
<tr>
<td>Actinoid chemistry</td>
<td>10</td>
</tr>
<tr>
<td>Actinochemistry separation</td>
<td>17</td>
</tr>
<tr>
<td>Others</td>
<td>3</td>
</tr>
<tr>
<td>Experiment used cold neutron</td>
<td>36</td>
</tr>
<tr>
<td>Experiment used thermal neutron</td>
<td>42</td>
</tr>
<tr>
<td>Medical or biological irradiation</td>
<td>2</td>
</tr>
<tr>
<td>Others</td>
<td>28</td>
</tr>
</tbody>
</table>

(Some numbers are overlapping)

43 out of 245 researchers do not intend to use research reactors in future because of reasons shown in Table 5.

Table 5 Reasons why researchers do not intend to use research reactors.

<table>
<thead>
<tr>
<th>Reason</th>
<th>Answers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Study finished</td>
<td>24</td>
</tr>
<tr>
<td>Another facility such as accelerator can be used</td>
<td>3</td>
</tr>
<tr>
<td>Budget is not estimated</td>
<td>3</td>
</tr>
<tr>
<td>Others</td>
<td>24</td>
</tr>
</tbody>
</table>

(Some numbers are overlapping)

2.3 Discussion in each utilization field

(1) Neutron activation analysis
Micro elements in various irradiation samples such as metals, animals, plants, water, soil and blood are analyzed by neutron activation analysis. This means that activation analysis can be used for general scientific fields such as environmental science, industry, biology or medical science. Therefore neutron activation analysis will be continued to use in accordance with the development of science and technology, and the investigated result also shows the same tendency on the activation analysis for very short life nuclide and prompt gamma ray analysis.

(2) Neutron scattering experiment
The neutron scattering experiments are used for the research of crystal structure, phase transition of material, lattice dynamics, magnetic structure, magnetic phase transition, spin dynamics and so on. The utilization of cold neutron makes it possible to research the reaction process in high polymer and cell structure, physiological activity in biological creature, etc.. The results can be understood that many research institutes which have not used research reactors, hope to do experiments on high polymer and biological creature. This means that studies of phase transition in high polymer and molecular structure, cell structure in biological creature are expected in future.

(3) Neutron radiography (NRG)
The NRG has been mainly utilized for limited research area such as irradiated fuel pin. On the other hand, 64 out of all answered questionnaires show that they have plans or interest for the utilization of new research using NRG. The expected new fields are general scientific fields such as general industry, agriculture, aviation and astronmatic.
(4) Silicon irradiation

Needs of neutron transmutation doping (NTD) silicon in the world is spoken to be about 160 tons per year in 1990 fiscal year, of which 70 percent is occupied by Japanese semiconductor makers. At present, the capacity of irradiation for NTD satisfies the needs of the world, however, capacity of them is foreseen to become scarce in near future because that the needs of NTD silicon in the world is expected to increase in the rate of 10 percent per year.

At the first stage of the silicon irradiation, the silicon diameter was mainly 3 inches, but now shifts to 4 or 5 inches. The investigation result shows that more than 5 inches of silicon diameter will be main needs in near future.

2.4 Other opinions

Some opinions for the utilization in research reactors of JAERI are also shown in the following.
- The chance of the exchange of users informations for utilization is few.
- The accommodation and supporting experimental facilities are necessary.
- The supports for the experimental technique, disposal treatment, etc are necessary.
- The organization for the utilization such as "Research reactor utilization center" is expected for the effective and high quality utilization.

3. CURRENT STATUS OF UTILIZATION IN JAERI

As shown in Fig.3, irradiation capsule numbers in research reactor of JAERI have decreased a little recently.

Fig.4 shows percentages of irradiation classified to purpose during 1991 fiscal year in the research reactors in JAERI.

Fig.5 shows available beam time on the universities' instruments and requested beam time from the universities. This figure shows that requested beam time in 1992 and 1993 already exceed available beam time extensively even in a few years after the completion of JRR-3M. This reason is considered to be the installation of many high performance experimental facilities including a cold neutron source and this leads to the extension of many kinds of research field.

![Fig.3 Number of irradiation capsules in research reactor of JAERI]
Fig. 4 Percentages of irradiation classified to purpose during 1991 fiscal year in the research reactors in JAERI

Fig. 5 Available beam time on the universities' instruments and requested beam time from the university users
4. CONCLUSION

From the investigation and the current status on research reactor utilization in JAERI, the following conclusions can be drawn.
- 23% of institutes which have not used research reactors, answered that they intended to use research reactors. This means that there will be many research institutes or users intending to use research reactor in Japan if they have adequate information for the utilization.
- It will make the research reactor utilization more active to arrange new utilization facilities and to open for users in the many kind of research fields.
- It is necessary to make a technical and human support of the experiments for effective utilization of research reactors.
- It is important for effective utilization of research reactors to satisfy user's new needs and to make the information open to researchers by the exchange of informations between users and staffs of facility side.
- It seems to be necessary to establish "the utilization center of research reactors" to carry out the items above mentioned.

ACKNOWLEDGEMENT

The authors wish to thank Executive Managing Director Komori and the staffs of Radiation Application Development Association for cooperating the investigation. We also wish to thank Dr. Kakurai of Tokyo University for his arrangement of universities' data.

REFERENCE

NEUTRON SCATTERING FACILITIES
FOR THE PROPOSED NEW RESEARCH REACTOR

J. BOLDEMAN, D. COOKSON, R.L. DAVIS, M.M. ELCOMBE,
C.J. HOWARD, S.J. KENNEDY, R. KNOTT and S.L. TOWN

Australian Nuclear Science & Technology Organization,
PMB1, Menai 2234, NSW

An inquiry is underway to determine whether on review of the benefits and costs for scientific, commercial, industrial and national interest reasons, Australia has a need for a new research reactor. If the Committee of Inquiry recommends in favour of the construction of a new research reactor, they will consider the question of an appropriate site. The research priorities for the new research reactor are neutron scattering research, radioisotope production and silicon irradiation. The configuration of the reactor would be optimized for neutron beam research and accordingly would have a small compact high intensity core. The reactor would also have hot and cold neutron sources. The proposed specification and instrumentation and planned research program will be presented.
## Authors Index

<p>| A | Abe, H. | P - 123 |
|   | Achiwa, N. | P - 151,304 |
|   | Aizawa, K. | P - 213,302,306,511 |
|   | Ajito, Y. | P - 124,125 |
|   | Akiba, E. | P - 104,117 |
|   | Akimoto, J. | P - 110,111 |
|   | Akine, Y. | P - 503 |
|   | Akiyoshi, T. | P - 304 |
|   | Andow, T. | P - 136 |
|   | Arai, M. | P - 103,113,138,157 |
|   | Asano, H. | P - 210,508 |
|   | Asano, T. | P - 101,124 |
|   | Ataka, M. | P - 209 |
|   | Atake, T. | P - 129 |
| B | Barton, J.P. | I - 16 |
|   | Boku, T. | P - 138 |
|   | Boldeman, J. | P - 611 |
|   | Brunner, T.M. | P - 203 |
| C | Child, H.R. | P - 146,157 |
|   | Chou, H. | P - 146 |
|   | Churel, H. | P - 503 |
|   | Clausen, K.N. | P - 116 |
|   | Cookson, D. | P - 611 |
| D | Date, M. | I - 1 |
|   | David, W.I.F. | P - 210 |
|   | Davis, R.L. | P - 611 |
|   | Donn, A. | P - 119,121 |
| E | Ebisawa, T. | P - 302,304,602 |
|   | Eguchi, M. | P - 412 |
|   | Elcombe, M.M. | P - 611 |
|   | Endler, M. | P - 116 |
|   | Endoh, T. | P - 513 |
|   | Endoh, Y. | I - 6, P - 103,113,118,119,128,140,157 |
| F | Fernandez-Baca, J.A. | P - 155 |
|   | Fischer, P. | P - 121 |
|   | Fruchart, D. | P - 117 |
|   | Fuchigaki, K. | P - 146,224 |
|   | Fuji, H. | P - 139 |
|   | Fuji, T. | P - 407 |
|   | Fujii, Y. | P - 151,304 |
|   | Fujikawa, S.I. | P - 214 |
|   | Fujime, S. | P - 402,405 |
|   | Fujishita, H. | P - 142 |
|   | Fujita, S. | P - 117 |
|   | Fuketa, T. | Summary Talk |
|   | Fukuda, K. | P - 156 |
|   | Funahashi, H. | P - 332 |
|   | Funahashi, S. | P - 104,108,109,111,112,115,136,141,142,143,144,146,147,150,154,155,156,158,202,216,224,226,512 |
|   | Furrer, A. | P - 121 |
|   | Furusaka, M. | P - 214 |
| H | Haga, Y. | P - 102,146 |
|   | Hajjiwood, A.K. | P - 414 |
|   | Harnaguchi, Y. | P - 112,226 |
|   | Han, C.C. | I - 10, P - 205,206,217,218,222 |
|   | Hannon, A.C. | P - 103,203 |
|   | Hasegawa, H. | I - 16, P - 205,221,222 |
|   | Hasegawa, Y. | P - 335 |
|   | Hashiguchi, R.R. | Short Note |
|   | Hashimoto, M. | P - 332 |
|   | Hashimoto, T. | P - 105,222 |
|   | Hatamura, H. | I - 4, P - 406,507 |
|   | Hayakawa, H. | P - 117 |
|   | Hayashi, M. | P - 512 |
|   | Hayter, J.B. | I - 21 |
|   | Hibi, T. | P - 405 |
|   | Hidaka, M. | P - 607 |
|   | Hidaka, Y. | P - 103 |
|   | Hino, M. | P - 304 |
|   | Hiraga, K. | P - 103,144 |
|   | Hirai, T. | P - 109 |
|   | Hirata, J. | P - 510 |
|   | Hoek, M. | P - 609 |
|   | Hoshi, M. | P - 409,410,414 |
|   | Hoshi, Y. | P - 610 |
|   | Hoshiba, S. | P - 123 |
|   | Hosoya, S. | P - 103,113,140 |
|   | Howard, C.J. | P - 131,611 |
|   | Huang, J. | P - 127 |
|   | Hutchings, M. | I - 18 |
| I | Ibberson, R.M. | P - 210 |
|   | Ichikawa, H. | P - 509,608 |
|   | Ichikawa, K. | P - 235 |
|   | Iizumi, K. | P - 513 |
|   | Iguchi, T. | P - 605 |
|   | Iijima, K. | P - 511 |
|   | Iizuka, K. | P - 412 |
|   | Izumi, M. | I - 2 |
|   | Ikeda, S. | P - 126,145,148,149 |
|   | Ikeda, H. | P - 130 |
|   | Inami, T. | P - 116,137 |
|   | Inui, M. | P - 219,220,502 |
|   | Iriyama, T. | P - 144 |
|   | Ishigaki, T. | P - 112 |
|   | Ishii, Y. | P - 156,158,159 |
|   | Ishikawa, K. | P - 605 |</p>
<table>
<thead>
<tr>
<th>Name</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ishiwata, M.</td>
<td>512</td>
</tr>
<tr>
<td>Ito, A.</td>
<td>165</td>
</tr>
<tr>
<td>Ito, Y.</td>
<td>222,223,409,410,414</td>
</tr>
<tr>
<td>Itô, S. (Tohoku)</td>
<td>116</td>
</tr>
<tr>
<td>Itô, S. (KEK)</td>
<td>118</td>
</tr>
<tr>
<td>Iversen, B. B.</td>
<td>133</td>
</tr>
<tr>
<td>Iwasa, H.</td>
<td>406</td>
</tr>
<tr>
<td>Iizumi, F.</td>
<td>104,129</td>
</tr>
<tr>
<td>Iizumi, Y.</td>
<td>218</td>
</tr>
<tr>
<td>Kiyanagi, Y.</td>
<td>406</td>
</tr>
<tr>
<td>Knott, R.</td>
<td>611</td>
</tr>
<tr>
<td>Kobayashi, H. (Electron)</td>
<td>136</td>
</tr>
<tr>
<td>Kobayashi, H. (Hiro)</td>
<td>602</td>
</tr>
<tr>
<td>Kobayashi, H. (Rikiyko)</td>
<td>411,413,504</td>
</tr>
<tr>
<td>Kobayashi, K.</td>
<td>144</td>
</tr>
<tr>
<td>Kobayashi, N.</td>
<td>108</td>
</tr>
<tr>
<td>Kobayashi, Y. (KURRI)</td>
<td>501,506</td>
</tr>
<tr>
<td>Kodaira, T.</td>
<td>803</td>
</tr>
<tr>
<td>Koga, T.</td>
<td>211</td>
</tr>
<tr>
<td>Kohgi, M.</td>
<td>102,120,139,141,148</td>
</tr>
<tr>
<td>Kohn, K.</td>
<td>115</td>
</tr>
<tr>
<td>Kojima, Y.</td>
<td>108</td>
</tr>
<tr>
<td>Koizumi, S.</td>
<td>221</td>
</tr>
<tr>
<td>Kojima, H.</td>
<td>113</td>
</tr>
<tr>
<td>Komatsu, H.</td>
<td>507</td>
</tr>
<tr>
<td>Komatsu, T.</td>
<td>119</td>
</tr>
<tr>
<td>Komura, S.</td>
<td>232,501,602</td>
</tr>
<tr>
<td>Konishi, A.</td>
<td>146</td>
</tr>
<tr>
<td>Kosaki, K.</td>
<td>504</td>
</tr>
<tr>
<td>Kotani, S.</td>
<td>215</td>
</tr>
<tr>
<td>Kayama, Y.</td>
<td>610</td>
</tr>
<tr>
<td>Kibota, S.</td>
<td>105</td>
</tr>
<tr>
<td>Kida, J.</td>
<td>139</td>
</tr>
<tr>
<td>Kumaizawa, S.</td>
<td>191,133</td>
</tr>
<tr>
<td>Kunitomi, N.</td>
<td>135</td>
</tr>
<tr>
<td>Kuriyama, H.</td>
<td>101,124</td>
</tr>
<tr>
<td>Kuroda, Y. (Tokyo)</td>
<td>129</td>
</tr>
<tr>
<td>Kuroda, Y. (Chiba)</td>
<td>145,508</td>
</tr>
<tr>
<td>Lander, G. H.</td>
<td>3</td>
</tr>
<tr>
<td>Lang, M.</td>
<td>149</td>
</tr>
<tr>
<td>Larsen, F. K.</td>
<td>133</td>
</tr>
<tr>
<td>Lehech, B.</td>
<td>151</td>
</tr>
<tr>
<td>Magara, M.</td>
<td>414</td>
</tr>
<tr>
<td>Makita, T.</td>
<td>150,154</td>
</tr>
<tr>
<td>Maruyama, K.</td>
<td>632</td>
</tr>
<tr>
<td>Mashiya, H.</td>
<td>122</td>
</tr>
<tr>
<td>Matsubayashi, M.</td>
<td>401,404,405,505</td>
</tr>
<tr>
<td>Matsumoto, G.</td>
<td>143</td>
</tr>
<tr>
<td>Matsumoto, H.</td>
<td>411</td>
</tr>
<tr>
<td>Matsumoto, K.</td>
<td>506,507</td>
</tr>
<tr>
<td>Matsumoto, S.</td>
<td>411</td>
</tr>
<tr>
<td>Matsumoto, T.</td>
<td>506</td>
</tr>
<tr>
<td>Matsuoka, T.</td>
<td>210</td>
</tr>
<tr>
<td>Matsushita, Y.</td>
<td>217,218</td>
</tr>
<tr>
<td>Mekata, M.</td>
<td>101,124</td>
</tr>
<tr>
<td>Mezaki, F.</td>
<td>22</td>
</tr>
<tr>
<td>Miyake, M.</td>
<td>238</td>
</tr>
<tr>
<td>Miki, H.</td>
<td>147</td>
</tr>
<tr>
<td>Minai, Y.</td>
<td>409,410</td>
</tr>
<tr>
<td>Minakawa, N.</td>
<td>512</td>
</tr>
<tr>
<td>Minezaki, Y.</td>
<td>209</td>
</tr>
<tr>
<td>Name</td>
<td>Page</td>
</tr>
<tr>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>Mino, M.</td>
<td>P-138</td>
</tr>
<tr>
<td>Minobe, M.</td>
<td>P-224</td>
</tr>
<tr>
<td>Minobe, T.</td>
<td>P-507</td>
</tr>
<tr>
<td>Miraglia, S.</td>
<td>P-117</td>
</tr>
<tr>
<td>Mishima, K.</td>
<td>P-405</td>
</tr>
<tr>
<td>Mishima, Y.</td>
<td>P-510</td>
</tr>
<tr>
<td>Mita, K.</td>
<td>P-208</td>
</tr>
<tr>
<td>Mitusa, S.</td>
<td>P-101, 102, 124</td>
</tr>
<tr>
<td>Mitsui, T.</td>
<td>P-408</td>
</tr>
<tr>
<td>Miyazaki, Y.</td>
<td>P-109</td>
</tr>
<tr>
<td>Mizobuchi, D.</td>
<td>P-604</td>
</tr>
<tr>
<td>Mizuki, J.</td>
<td>P-128</td>
</tr>
<tr>
<td>Mizuki, H.</td>
<td>P-225</td>
</tr>
<tr>
<td>Mogi, Y.</td>
<td>P-217, 218</td>
</tr>
<tr>
<td>Moon, R.M.</td>
<td>P-135</td>
</tr>
<tr>
<td>Mori, K.</td>
<td>P-112</td>
</tr>
<tr>
<td>Mori, N.</td>
<td>P-102, 148, 155</td>
</tr>
<tr>
<td>Morii, Y.</td>
<td>I-8, P-104, 108, 109, 114, 121, 143</td>
</tr>
<tr>
<td>Morisako, T.</td>
<td>P-607</td>
</tr>
<tr>
<td>Morishima, N.</td>
<td>P-604</td>
</tr>
<tr>
<td>Mortensen, K.</td>
<td>P-292</td>
</tr>
<tr>
<td>Moss, S.C.</td>
<td>P-145</td>
</tr>
<tr>
<td>Motokawa, M.</td>
<td>P-137, 138</td>
</tr>
<tr>
<td>Motoya, K.</td>
<td>P-105</td>
</tr>
<tr>
<td>Murakami, S.</td>
<td>P-508</td>
</tr>
<tr>
<td>Murayama, C.</td>
<td>P-155</td>
</tr>
<tr>
<td>Naka, Y.</td>
<td>P-212</td>
</tr>
<tr>
<td>Nakaniishi, T.M.</td>
<td>P-411</td>
</tr>
<tr>
<td>Nakazawa, M.</td>
<td>P-606</td>
</tr>
<tr>
<td>Nakazawa, T.</td>
<td>P-407</td>
</tr>
<tr>
<td>Naito, D.</td>
<td>P-610</td>
</tr>
<tr>
<td>Naito, H.</td>
<td>P-601</td>
</tr>
<tr>
<td>Naito, R.M.</td>
<td>P-107, 135, 158</td>
</tr>
<tr>
<td>Nishihara, N.</td>
<td>P-297, 206, 209</td>
</tr>
<tr>
<td>Nishi, M.</td>
<td>P-110, 114, 607</td>
</tr>
<tr>
<td>Nakanishi, T.</td>
<td>P-606</td>
</tr>
<tr>
<td>Noda, L.</td>
<td>P-217, 218</td>
</tr>
<tr>
<td>Noda, Y.</td>
<td>P-145, 146, 508</td>
</tr>
<tr>
<td>Noji, T.</td>
<td>P-108</td>
</tr>
<tr>
<td>Nomura, M.</td>
<td>P-217</td>
</tr>
<tr>
<td>Oda, M.</td>
<td>P-404</td>
</tr>
<tr>
<td>Oda, Y.</td>
<td>P-301</td>
</tr>
<tr>
<td>Ohara, K.</td>
<td>P-403</td>
</tr>
<tr>
<td>Ohhashi, M.</td>
<td>P-136, 143, 903</td>
</tr>
<tr>
<td>Ohishi, Y.</td>
<td>P-224</td>
</tr>
<tr>
<td>Ohkubo, K.</td>
<td>P-304</td>
</tr>
<tr>
<td>Ohkubo, M.</td>
<td>P-305</td>
</tr>
<tr>
<td>Ohno, H.</td>
<td>I-11, P-154, 158</td>
</tr>
<tr>
<td>Ohnuma, M.</td>
<td>P-228</td>
</tr>
<tr>
<td>Ohoyama, K.</td>
<td>P-139, 147, 152</td>
</tr>
<tr>
<td>Ohshina, K.</td>
<td>P-123</td>
</tr>
<tr>
<td>Ohtomo, S.</td>
<td>P-405</td>
</tr>
<tr>
<td>Okamura, K.</td>
<td>P-223</td>
</tr>
<tr>
<td>Okawara, Y.</td>
<td>P-102</td>
</tr>
<tr>
<td>Okumura, K.</td>
<td>P-303</td>
</tr>
<tr>
<td>Ono, T.</td>
<td>P-113, 130</td>
</tr>
<tr>
<td>Ono, A.</td>
<td>P-407</td>
</tr>
<tr>
<td>Ono, K.</td>
<td>P-510</td>
</tr>
<tr>
<td>Ono, T.</td>
<td>P-136</td>
</tr>
<tr>
<td>Onoda-Yamamura, N.</td>
<td>P-210</td>
</tr>
<tr>
<td>Onodera, A.</td>
<td>P-135, 151</td>
</tr>
<tr>
<td>Onodera, H.</td>
<td>P-136, 143</td>
</tr>
<tr>
<td>Onuki, Y.</td>
<td>P-120, 141</td>
</tr>
<tr>
<td>Oohara, Y.</td>
<td>P-101, 102, 122, 124</td>
</tr>
<tr>
<td>Oomi, G.</td>
<td>P-605</td>
</tr>
<tr>
<td>Osaka, T.</td>
<td>P-102, 120, 139, 141, 148, 152, 153</td>
</tr>
<tr>
<td>Otomo, T.</td>
<td>P-132</td>
</tr>
<tr>
<td>Oyamada, A.</td>
<td>P-132</td>
</tr>
<tr>
<td>Ozaki, Y.</td>
<td>P-132</td>
</tr>
</tbody>
</table>

< N >
<p>| Nagai, M.   | P-602 |
| Nagasawa, A. | P-130, 154 |
| Nakagawa, Y. (Tokio) | P-144 |
| Nakagawa, Y. (Kagawa) | P-506, 507 |
| Nakai, Y. (Shizuoka) | P-151 |
| Nakai, Y. (Tsukuba) | P-508 |
| Nakajima, K. | P-113, 116, 140 |
| Nakamura, H. (Kyoto) | P-114 |
| Nakamura, H. (Tokio) | P-501 |
| Nakamura, Y. | P-212 |
| Nakasuga, Y. | P-406 |
| Nakata, Y.   | P-508 |
| Nakai, K.    | P-131, 133 |
| Nakamura, Y. | P-505 |
| Naka, Y.     | P-510 |
| Nakanishi, T. | P-140 |
| Noda, T.     | P-142 |
| Noda, N.     | P-119, 120 |
| Noda, Y.     | P-134 |
| Noda, S.     | P-503 |
| Nogami, H.   | P-404 |
| Nogami, R.   | P-202 |
| Nogami, T.   | P-203 |
| Nogami, T.   | P-301 |
| Serizawa, H. | P-155 |</p>
<table>
<thead>
<tr>
<th>Name</th>
<th>Page Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seto, H.</td>
<td>P-202, 601, 602</td>
</tr>
<tr>
<td>Shibata, K.</td>
<td>P-149, 212, 225</td>
</tr>
<tr>
<td>Shibayama, M.</td>
<td>P-206</td>
</tr>
<tr>
<td>Shigeta, M.</td>
<td>P-114</td>
</tr>
<tr>
<td>Shimizu, T.</td>
<td>P-149</td>
</tr>
<tr>
<td>Shirizumi, H.M.</td>
<td>P-301</td>
</tr>
<tr>
<td>Shinomura, S.</td>
<td>Opening Address</td>
</tr>
<tr>
<td>Shiokaki, Y.</td>
<td>P-605</td>
</tr>
<tr>
<td>Shirakawa, Y.</td>
<td>P-219, 220</td>
</tr>
<tr>
<td>Shirane, G.</td>
<td>I-5</td>
</tr>
<tr>
<td>Siratori, K.</td>
<td>P-110, 111</td>
</tr>
<tr>
<td>Sleight, A.W.</td>
<td>P-127</td>
</tr>
<tr>
<td>Sobajima, M.</td>
<td>P-405</td>
</tr>
<tr>
<td>Soloway, A.H.</td>
<td>P-501</td>
</tr>
<tr>
<td>Soubeyroux, J.L.</td>
<td>P-117</td>
</tr>
<tr>
<td>Soyama, K.</td>
<td>P-509, 608</td>
</tr>
<tr>
<td>Steiner, M.</td>
<td>P-116</td>
</tr>
<tr>
<td>Kraen, D.</td>
<td>P-139</td>
</tr>
<tr>
<td>Sugi, H.</td>
<td>P-210</td>
</tr>
<tr>
<td>Sugimoto, K.</td>
<td>P-122</td>
</tr>
<tr>
<td>Sugiyama, K.</td>
<td>P-219, 220</td>
</tr>
<tr>
<td>Sunagawa, H.</td>
<td>P-108</td>
</tr>
<tr>
<td>Suzuki, J.</td>
<td>P-157, 202, 216, 221, 224, 226</td>
</tr>
<tr>
<td>Suzuki, K.</td>
<td>P-212, 223, 225</td>
</tr>
<tr>
<td>Suzuki, M.</td>
<td>P-509, 608</td>
</tr>
<tr>
<td>Suzuki, T. (Tohoku)</td>
<td>P-102, 121, 148, 152</td>
</tr>
<tr>
<td>Suzuki, T. (Tsukuba)</td>
<td>P-123, 125</td>
</tr>
<tr>
<td>Suzuki, Y.</td>
<td>P-223</td>
</tr>
<tr>
<td>Tanaka, J. (Hokkaido)</td>
<td>P-208</td>
</tr>
<tr>
<td>Tanaka, T.</td>
<td>P-206</td>
</tr>
<tr>
<td>Tasaka, K.</td>
<td>P-404</td>
</tr>
<tr>
<td>Tatsuki, S.</td>
<td>P-302, 304, 602</td>
</tr>
<tr>
<td>Taylor, A.D.</td>
<td>I-7.20, P-103, 113</td>
</tr>
<tr>
<td>Terai, M.</td>
<td>P-402</td>
</tr>
<tr>
<td>Todate, Y.</td>
<td>P-130</td>
</tr>
<tr>
<td>Tokita, N.</td>
<td>P-503</td>
</tr>
<tr>
<td>Tokunaga, F.</td>
<td>P-206</td>
</tr>
<tr>
<td>Tokunaga, K.</td>
<td>P-503</td>
</tr>
<tr>
<td>Tomimatsu, H.</td>
<td>P-213, 302, 306, 511</td>
</tr>
<tr>
<td>Tominaga, T.</td>
<td>P-409, 410</td>
</tr>
<tr>
<td>Tomita, T.</td>
<td>P-504</td>
</tr>
<tr>
<td>Tomiyoshi, S.</td>
<td>P-130, 147</td>
</tr>
<tr>
<td>Tomizawa, T.</td>
<td>P-410</td>
</tr>
<tr>
<td>Tomomura, A.</td>
<td>I-14</td>
</tr>
<tr>
<td>Torikai, N.</td>
<td>P-288</td>
</tr>
<tr>
<td>Town, S.L.</td>
<td>P-611</td>
</tr>
<tr>
<td>Toyota, N.</td>
<td>P-118, 149</td>
</tr>
<tr>
<td>Tranquand, J.M.</td>
<td>P-214</td>
</tr>
<tr>
<td>Tsutji, F.</td>
<td>P-507</td>
</tr>
<tr>
<td>Tsudera, Y.</td>
<td>P-107, 135</td>
</tr>
<tr>
<td>Tsuruno, A.</td>
<td>P-401, 404, 405, 407, 411, 505</td>
</tr>
</tbody>
</table>

<U>
| Ubukata, K.          | P-137, 138 |
| Ueda, Y.             | P-155 |
| Uemura, A.           | P-224 |
| Umesaki, N.          | P-238 |
| Uno, T.              | P-131 |
| Usui, Y.             | P-225 |
| Usuki, T.            | P-219, 220 |
| Utsuro, M.           | I-15, P-303 |

<W>
| Wakita, H.           | P-211 |
| Waseda, Y.           | P-218, 220, 502 |
| Watanabe, J.         | P-279 |
| Watanabe, T.         | P-118, 128 |
| Wright, A.C.         | P-209 |

<Y>
| Yaguchi, N.          | P-101, 124 |
| Yamada, K.           | P-163, 113, 118, 128, 140 |
| Yamada, N.           | P-115 |
| Yamada, Y.           | P-145, 146 |
| Yamagami, M.         | P-211 |
| Yamaguchi, T.        | P-211 |
| Yamaguchi, Y.        | P-126, 136, 143, 147 |
| Yamamoto, O.         | P-129 |
| Yamamoto, Y.         | P-301 |
| Yamamura, O.         | P-210 |
| Yamauchi, H.         | P-109 |
| Yamauchi, Y.         | P-301 |
| Yamauchi, H.         | P-143 |
| Yamauchi, R.         | P-150 |
| Yanagie, H.          | P-504 |

--- 1030 ---
Yasuda, H. P-128
Yasunishi, A. P-411
Yazaki, A. P-130
Yokoi, E. P-222, 602
Yoneda, K. P-402, 405
Yonezawa, C. P-409, 410, 414
Yonezu, I. P-117
Yoshinari, A. P-311
Yoshizawa, H. P-101, 102, 105, 122, 124
Yoshizawa, Y. P-141

(Z)
Zaccari, G. I-12
Zhang, Z.H. P-501