~~LANSCE~~

*The Manuel Lujan, Jr.
Neutron Scattering Center
Experiment Reports
1992 Run Cycle*

L. Sanchez

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

*Prepared by Alix Krakowski, LANSCE
Design by Gail Flower, Group IS-1*

Photography by John Flower, Group IS-9

*The most recently published reports in this series,
unclassified, are LA-11638-PR, LA-11933-PR,
LA-12194-PR, and LA-12407-PR.*

*This work was supported
by the US Department of Energy,
Office of Energy Research.*

An Affirmative Action/Equal Opportunity Employer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither The Regents of the University of California, the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by The Regents of the University of California, the United States Government, or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of The Regents of the University of California, the United States Government, or any agency thereof.

LA-12647-PR
Progress Report

UC-410 and UC-404
Issued: September 1993

*The Manuel Lujan, Jr.
Neutron Scattering Center (LANSCE)
Experiment Reports
1992 Run Cycle*

*Compiled by
Maria A. DiStravolo*

Los Alamos
NATIONAL LABORATORY

Los Alamos, New Mexico 87545

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

for

Contents

<i>Abstract</i>	<i>vii</i>
<i>LANSCE Highlights</i>	<i>1</i>
<i>User Program</i>	<i>7</i>
<i>Users visiting LANSCE during 1992</i>	<i>11</i>
<i>High Intensity Powder Diffractometer (HIPD)</i>	<i>13</i>
<i>Experiment reports</i>	<i>17</i>
<i>Neutron Powder Diffractometer (NPD)</i>	<i>49</i>
<i>Experiment reports</i>	<i>53</i>
<i>Single Crystal Diffractometer (SCD)</i>	<i>85</i>
<i>Experiment reports</i>	<i>89</i>
<i>Low-Q Diffractometer (LQD)</i>	<i>105</i>
<i>Experiment reports</i>	<i>109</i>
<i>Surface Profile Analysis Reflectometer (SPEAR)</i>	<i>135</i>
<i>Experiment reports</i>	<i>139</i>
<i>Filter Difference Spectrometer (FDS)</i>	<i>177</i>
<i>Experiment reports</i>	<i>181</i>
<i>PHAROS</i>	<i>191</i>
<i>Appendices</i>	<i>195</i>
<i>Distinguished Performance Award</i>	<i>197</i>
<i>Publication list</i>	<i>198</i>
<i>Author index</i>	<i>208</i>
<i>Subject index</i>	<i>211</i>

Abstract

This year was the fifth in which LANSCE ran a formal user program. A call for proposals was issued before the scheduled run cycles, and experiment proposals were submitted by scientists from universities, industry, and other research facilities around the world. An external program advisory committee, which LANSCE shares with the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, examined the proposals and made recommendations.

At LANSCE, neutrons are produced by spallation when a pulsed, 800-MeV proton beam impinges on a tungsten target. The proton pulses are provided by the Clinton P. Anderson Meson Physics Facility (LAMPF) accelerator and an associated Proton Storage Ring (PSR), which can alter the intensity, time structure, and repetition rate of the pulses. The LAMPF protons of Line D are shared between the LANSCE target and the Weapons Neutron Research (WNR) facility, which results in LANSCE spectrometers being available to external users for unclassified research about 80% of each annual LAMPF run cycle. Measurements of interest to the Los Alamos National Laboratory may also be performed and may occupy up to an additional 20% of the available beam time. These experiments are reviewed by an internal program advisory committee. One hundred sixty-seven proposals were submitted for unclassified research and twelve proposals for research of a programmatic interest to the Laboratory; six experiments in support of the LANSCE research program were accomplished during the discretionary periods. Oversubscription for instrument beam time by a factor of three was evident with 839 total days requested and only 371 available for allocation.

Proposals

RN 92 033 017

LANSCE Highlights

Overview

The Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) is a pulsed spallation neutron source equipped with time-of-flight spectrometers for condensed-matter research. Neutron scattering is a powerful technique for probing the microscopic structure of condensed matter. Both the energies and wavelengths of thermal neutrons closely match typical excitation energies and interatomic distance in solids and liquids. Because neutrons have no charge, they penetrate bulk samples of material to give precise information on the position and motions of individual atoms. The magnetic moment of a neutron interacts with unpaired electrons, making neutrons ideal for probing microscopic magnetic properties. Because neutron-scattering cross sections do not vary in a systematic manner with the atomic number of the scattering nucleus, neutrons and x-rays can provide complementary structural information. This technique is particularly effective for structural problems in biological studies; both hydrogen and deuterium scatter neutrons strongly but with different cross sections.

LANSCE offers a range of instruments for determining the atomic and magnetic structure and dynamics of polycrystalline and crystalline materials, such as high-temperature superconductors, pharmaceuticals, and polymers; and the structure of molecular coatings of solid and liquid surfaces.

One instrument at LANSCE—a powder diffractometer—has a higher resolution than any other instrument of its type in the United States. Important industrial uses of the facility include the measurement of residual stress in metals, ceramics, and composites; the determination of texture in metals and alloys; the characterization of void and precipitate sizes in alloys and ceramics; and the examination of layer structure of protective surface coatings.

At LANSCE, neutrons are produced by spallation when a pulsed, 800-million-electron-volt proton beam impinges on a tungsten target. The pulses are provided by the Clinton P. Anderson Meson Physics Facility (LAMPF) accelerator and an associated Proton Storage Ring (PSR), which can alter the intensity, time structure, and repetition rate of the pulses. Spallation produces neutrons of relatively high energy, so moderators adjacent to the target must be used to reduce the energies to those required for condensed-matter research. Because of the unique design of the split-target, flux-trap moderator, reflector-shield, LANSCE yields a higher neutron beam flux than any other spallation neutron source used for condensed-matter research. This means that scientists can perform experiments more quickly, more accurately, and with smaller samples at LANSCE than at any other similar facility.

LANSCE Target-Moderator System

Mission

The Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) is a pulsed-spallation neutron source for neutron-scattering investigations in physics, chemistry, biology, and materials science. A DOE-sponsored facility, LANSCE has two main missions: it serves as a national user facility with peer-reviewed access for scientists from academia, federal laboratories, and industry; and it is a resource for condensed-matter researchers at Los Alamos.

To support its primary missions, LANSCE

- designs and builds new and powerful neutron-scattering spectrometers,
- designs and builds targets/moderator systems for optimal production of neutrons,
- designs and builds electronic and computer hardware and software for data acquisition and analysis,
- performs forefront research in neutron scattering,
- assists users of the facility during data collection and analysis,
- promotes the application of neutron-scattering techniques to new areas of science and technology, and
- provides an educational resource for undergraduate and graduate students.

An artist's conception of the proton beam from LAMPF (1) feeding into the PSR (2), which then sends it to the LANSCE neutron production target (3). The support building (5) is shown on the right.

Student Programs

Students are an active part of the operational and organizational elements of LANSCE. Students from local high schools and undergraduate and graduate programs from around the world have the opportunity to learn aspects of experimental design and instrumentation; computer simulation; computer programming; data and numerical analysis; and administrative office operation, which includes office management, technical design and illustration, and organizational development. Student appointments range from 90 days to one year (with possible extensions depending on funding and programmatic impact). LANSCE encourages students to work independently and to develop their ideas to fruition.

Student employment is coordinated through the Human Resources Division Special Programs Office (HRD-2) and Community Outreach (HRD-5). Some of the programs at the Laboratory are

- Science and Technology Alliance (STA)
- Science and Engineering Research Semester (SERS)
- Service Academies Research Associates (SARA)

- Historically Black Colleges and Universities Program (HBCU)
- High School Co-operative Program
- Undergraduate Student Program
- Graduate Research Associate
- Special Education Working Experience Program (SWEP)
- Internships Programs

In addition, LANSCE participates in the Laboratory's Postdoctoral Research Program. Postdoctoral candidates must have received their doctoral degree less than three years before the appointment at LANSCE. Candidates are nominated by LANSCE scientists and reviewed by a Laboratory-wide committee before the awards are given.

Each appointment is for a period of two years, with a discretionary third year for researchers with good potential. The post doctoral program is active; the Laboratory views it as a means of attracting new scientific talent. LANSCE supplements this program by paying part or all of the overhead for suitably qualified candidates.

Students and post docs

RB 92045 022

RB 92064 006

RB 92045 029

LANSCE file photo

Upper left: Paul Romero, an undergraduate at the University of New Mexico, reviews the installation plans for the PHAROS detectors. Upper right: Kristin Bennett, a doctoral candidate at UC Berkeley, adjusts the valving on the nitrogen cryostat on NPD. Lower left: A Los Alamos post doc, Simon Billinge, notes the sample position change in the sample chamber on NPD. Lower right: Fabian Macias (top), a graduate student from Highlands University, and Phil Seeger analyze data taken from LQD.

RB 92/45 632

User Program

User Program

Research programs at LANSCE cover a broad range: solid-state physics, chemistry, metallurgy, crystallography, structural biology, materials science, and nuclear physics. About 80% of the available beam is intended for unclassified, nonproprietary research, and the remaining 20% is for support of the Laboratory's programmatic mission. Of the time available for condensed-matter research, three-quarters is distributed to a

formal user program. Advice on experiments to be performed in this category is provided by the external program advisory committee. DOE cost-recovery rules apply to proprietary experiments. LANSCE sponsors participating research teams (PRT), which are guaranteed access to a beam line for a negotiated period in exchange for financial participation in constructing a neutron spectrometer or ancillary equipment.

Kurt Leinenweber (left) and Donald J. Weidner of State University of New York at Stony Brook marvel at the data collected from a high-pressure (95 kbar) experiment done on brucite (magnesium hydroxide) using HIPD.

Instrument days requested

LANSCe file photo

Mike James of Rockwell International Science Center calculates residual strains in metal-ceramic laminates (alumina-alumina) from data collected on the NPD.

PUB-86111-60

A LANSCE associate, Angus Lawson of MST-5 (Materials Research and Processing Science) mounts an x-ray diffraction sample at the Center for Materials Research facility.

Users visiting LANSCE during 1992

Last name	First	Affiliation	Country
Albinati	Alberto	Universita di Milano	Italy
Allison	John	Ford Motor Company	USA
Aranda	Miguel	University of Cambridge	United Kingdom
Argyriou	Dimitri	Australian Nuclear Science & Technology Org.	Australia
Barthes	Mariette	Universite des Sciences et Techniques du Languedoc	France
Beaucage	Greg	Sandia National Laboratories	USA
Berman	Alan	University of California - Santa Barbara	USA
Besson	J.	LASIR Centre National Recherche Scientifique	France
Brisson	Catherine	LASIR Centre National Recherche Scientifique	France
Burke	Matthew	University of Technology - Sydney	Australia
Burkel	Eberhard	Universität München	Germany
Butler	Paul	University of Tennessee - Knoxville	USA
Cooper	Elizabeth	Los Alamos National Laboratory	USA
Curro	Nick	Sandia National Laboratories	USA
Dreux	Peter	University of Pennsylvania	USA
Egami	Takeshi	University of Pennsylvania	USA
Elcombe	Margaret	Australian Nuclear Science & Technology Org.	Australia
Forsman	W.	University of Pennsylvania	USA
Gill	Richard	University of Groningen	The Netherlands
Glaeser	Robert	University of California - Berkeley	USA
Gratz	Andrew	Lawrence Livermore National Laboratory	USA
Gray	George	Los Alamos National Laboratory	USA
Hamel	Gerard	Universite de Paris VI	France
Hamilton	William	Oak Ridge National Laboratory	USA
Harrison	William	University of Houston	USA
Heidelbach	Florian	Los Alamos National Laboratory	USA
Hellstrom	Eric	University of Wisconsin - Madison	USA
Hoffer	James	Los Alamos National Laboratory	USA
Hurd	Alan	Sandia National Laboratories	USA
Imai	Brian	Los Alamos National Laboratory	USA
Jayasooriya	U.	University of East Anglia	United Kingdom
Kalceff	Walter	University of Technology - Sydney	Australia
Kamiyama	Takashi	University of Tsukuba - Tennodai	Japan
Kearley	Gordon	Institut Laue Langevin	France
Kent	Michael	Sandia National Laboratories	USA
Klotz	Stefan	Universite de Paris VI	France
Kuhl	Tonya	University of California - Santa Barbara	USA
Kumar	Satyen	Kent State University	USA
Kuppers	Horst	Universität Kiel	Germany
Loveday	John	University of Edinburgh	Scotland
Maddaford	Paul	University of Cambridge	United Kingdom
Magnera	Thomas	University of Colorado	USA
Mang	Joseph	Kent State University	USA
Marking	Greg	Iowa State University	USA
Martin	J.	Sandia National Laboratories	USA
Martino	Tony	Sandia National Laboratories	USA
Mayes	Anne	MIT	USA

Last name	First	Affiliation	Country
Nakotte	Heinrich	Van der Waals-Zeeman Laboratorium	The Netherlands
Odinek	Judy	Sandia National Laboratories	USA
Olah	Glenn	Los Alamos National Laboratory	USA
Parise	John	State University of New York - Stony Brook	USA
Pruss	Eugene	University of California - Berkeley	USA
Reis	Kenneth	University of Houston	USA
Robl	Christian	Universität München	Germany
Rossetti	George	Princeton University	USA
Russell	Thomas	IBM	USA
Rzeznik	Maria	University of California - Berkeley	USA
Sabine	Terence	Australian Nuclear Science & Technology Org.	Australia
Salazar	Mike	Los Alamos National Laboratory	USA
Schmidt	Paul	University of Missouri - Columbia	USA
Schmitt	Franz-Josef	University of California - Santa Barbara	USA
Sosnick	Tobin	Los Alamos National Laboratory	USA
Steinberg	Suzi	University of California - Santa Barbara	USA
Straty	Gerald	National Institute of Standards & Technology	USA
Stride	John	University of East Anglia	United Kingdom
Swope	R. Jeffrey	University of Colorado	USA
Triebes	Thomas	University of Colorado	USA
Vigil	Fidel	Los Alamos National Laboratory	USA
Wilcoxon	Jess	Sandia National Laboratories	USA
Wilson	Charles	Rutherford Appleton Laboratory	United Kingdom
Wilson	Rory	University of Edinburgh	Scotland
Wlassich	John	MIT	USA
Yau	Peter	University of California - Davis	USA
Yoshizawa	Hisae	University of California - Santa Barbara	USA
Young	Victor	Iowa State University	USA
Zhang	Jie	Arizona State University	USA
Zocco	Thomas	Los Alamos National Laboratory	USA

R8 92 045 016

*High Intensity Powder
Diffractometer (HIPD)*

High Intensity Powder Diffractometer (HIPD)

The High Intensity Powder Diffractometer (HIPD) is designed to study the atomic structures of materials that are available only in polycrystalline or noncrystalline form. In the HIPD, the pulsed neutron beam is directed through a collimator onto a cylindrical or flat plate sample supported in a vacuum chamber. Neutrons are detected by banks of detectors located at various angles to the incident beam. The data from each detector are collected as a function of time of flight (TOF) and stored in a FASTBUS memory module, which is controlled by a micro-VAX II computer. Because the neutron TOF is directly proportional to the neutron wavelength, the measured diffraction pattern yields exact information on the atomic

arrangement in the sample. The HIPD offers exceptionally high data rates with nearly three decades of range in momentum transfer or d-spacing. An ambient-temperature, high-intensity water moderator provides a usable neutron flux at wavelengths out to 10 Å. Low backgrounds permit the routine use of wavelengths down to 0.2 Å. The HIPD is intended primarily for studies of liquids and amorphous solids, for magnetic diffraction studies, and for crystallographic studies of samples that are either very small or are in extreme environments of temperature, pressure, or magnetic fields. This instrument is also appropriate for experiments that require time-resolved diffraction measurements.

Instrument Details

Wavelength range, λ	0.20 - 10.0 Å
Beam width	1.0 - 0.3 cm, variable
Beam height	2.54 - 5.08 cm, variable 5.0 - 0.3 cm, variable
Q range	0.1 - 60 Å ⁻¹
Range of scattering angle	5° - 153°
Moderator	Chilled water at 10° C
Sample environment	13 - 300 K, closed cycle refrigerator
Sample size	0.005 - 4 cm ³
Experiment duration	5 minutes - 1 day, depending on sample size

Robert Von Dreele, instrument scientist
Eric Larson, instrument technician

HIPD Experiment reports

5001	<i>Crystal Structure Determination of UCu_3Al_2</i>	18
5004	<i>Magnetic and Structural Properties of UIrGe</i>	20
5010	<i>Neutron Scattering Investigation of Non-ideal Behavior of Binary Liquid Mixtures Using Contrast Variation</i>	22
5035	<i>Experimental Evaluation of Extinction and Absorption Theories for Neutron Time-of-Flight Diffraction</i>	23
5013	<i>Crystal Structure of the $8.4\text{\AA}$ Kaolinite-Hydrate Complex</i>	24
5037	<i>Pressure Dependence of Antiferromagnetic Moment in CeRh_2Si_2</i>	26
5046	<i>Report on "A New Approach to Neutron Texture Measurements Profile Analysis and Combination with Structure Refinements"</i>	28
5052	<i>Radial Distribution Function of Liquid Gallium</i>	30
5065	<i>Structural Characterization of $\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ by Neutron Powder Diffraction</i>	32
5066	<i>Pair Distribution Function Study of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$</i>	34
5077	<i>Determination of Hafnium/Tantalum and Sulfur/Oxygen Occupancies in New Mixed Metal Sulfides</i>	36
5116	<i>Local Atomic Structure of Solid Rb_3C_{60}</i>	38
5129	<i>Structure of Calcium-Ammonia Solvation Complexes Within Titanium Disulfide</i>	40
5133	<i>Crystal and Magnetic Structures of LiMnXO_4 (OD), MnAsO_4, and LiMnXO_4 (X=P, As)</i>	42
5146	<i>The Equation of State of Boron</i>	44
5405	<i>Debye-Waller Factors of α-Plutonium</i>	46

Instrument used: <i>(please type)</i> HIPD	Local contact: R. A. Robinson	Proposal number: <i>(for LANSCE use only)</i> 5001																									
Title: Crystal structure determination of UCu₃ Al₂		Report received: <i>(for LANSCE use only)</i> 7/29/93																									
Authors and affiliations: <p>H. Nakotte, F. R. de Boer, E. Bruck; University of Amsterdam</p> <p>R.A. Robinson, A. Purwanto; LANSCE</p>																											
Experiment report: <p>The compounds UCu₃Al₂ and UCu_{3.5}Al_{1.5} have been claimed to exhibit heavy fermion behaviour with an electronic contribution to the specific heat of about 400 mJ/molK² and 380 mJ/molK², respectively /1/. Both compounds were thought to crystallize in the hexagonal CaCu₅ structure (space group P6/mmm) with the Cu and Al atoms randomly distributed on the Cu sites. Assuming a random occupation of the 2c and 3g sites in the CaCu₅ structure one should expect no discontinuity in preparing compounds with Cu concentrations intermediate between 3 and 3.5. Preliminary results on intermediate compositions, however, show that compounds with x=3.2 and x=3.3 do not form in a single phase. Therefore a change or a modification of the crystal structure is to be expected. As UCu_{3.5}Al_{1.5} crystallizes in the disordered CaCu₅ structure, changes from this structure are to be expected for UCu₃Al₂. Furthermore the question whether the low-temperature anomaly observed in specific-heat, susceptibility and electrical resistivity measurements at about 8-12K for UCu₃Al₂ has a magnetic origin will be the basis for future experiments.</p> <p>In order to determine the crystallographic structure we took neutron diffraction data at room temperature. Using the program GSAS we were able to prove unambiguously, that an ordered structure with the 2c sites of the CaCu₅ structure occupied by Cu and the 3g sites occupied by Al and the remaining third of Cu is preferred. For this structure we obtained a value of 4.698 for reduced χ^2, while the best fit for the completely disordered structure yields in value of 14.9. The atomic positions for UCu₃Al₂ are:</p> <table border="1"> <thead> <tr> <th></th> <th>x</th> <th>y</th> <th>z</th> <th>frac</th> </tr> </thead> <tbody> <tr> <td>U</td> <td>0</td> <td>0</td> <td>0</td> <td>1</td> </tr> <tr> <td>Cu₁</td> <td>1/3</td> <td>2/3</td> <td>0</td> <td>1</td> </tr> <tr> <td>Cu₂</td> <td>1/2</td> <td>0</td> <td>1/2</td> <td>1/3</td> </tr> <tr> <td>Al</td> <td>1/2</td> <td>0</td> <td>1/2</td> <td>2/3</td> </tr> </tbody> </table>				x	y	z	frac	U	0	0	0	1	Cu ₁	1/3	2/3	0	1	Cu ₂	1/2	0	1/2	1/3	Al	1/2	0	1/2	2/3
	x	y	z	frac																							
U	0	0	0	1																							
Cu ₁	1/3	2/3	0	1																							
Cu ₂	1/2	0	1/2	1/3																							
Al	1/2	0	1/2	2/3																							

Experiment report (continued):

Figure 1: Portions of diffraction patterns from UCU3Al₂ taken at room temperature in one of the banks of HIPD. The solid line in the upper plot represents the fit for the ordered crystal structure mentioned above, while the solid line in the lower plot represents the fit for the completely disordered structure. Note the poor fit for the disordered structure especially for the reflections indicated by an arrow.

References:

/1/ H. Nakotte et. al, 20^{èmes} Journées des Actinides, April 1990, Prague, CSFR

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>																		
HIPD	R.A. Robinson	5004																		
Title:		Report received: <i>(for LANSCE use only)</i>																		
Magnetic and structural properties of UIrGe		7/29/93																		
Authors and affiliations:																				
<p>H. Nakotte, F. R. de Boer; University of Amsterdam</p> <p>K.H.J. Buschow; Philips Research Laboratories; Eindhoven</p> <p>V. Sechovsky, L. Havela; Charles University; Prague</p> <p>R.A. Robinson, A. Purwanto; LANSCE</p>																				
Experiment report:																				
<p>This work is part of a program to study the magnetic properties of ternary (1:1:1) uranium intermetallic compounds. Varying the degree of 5f-d hybridization for compounds forming in the same crystallographic structure, by moving across or down in the periodic table, leads to a progress from itinerant magnetism towards the formation of localized 5f moments /1/. The series UTSi and UTGe (T = transition metal) were found to crystallize in the orthorhombic CeCu₂ structure (space group: Imma). UPtGe, which belongs to the latter series, was already studied at LANSCE. This compound exhibits a cycloidal structure with an uranium moment of 0.98 μ_B and a propagation vector of (0,0.554,0) /2/. Similar results have been reported by a Japanese group, which studied UPdGe and UNiGe /3/.</p> <p>In this experiment we concentrated on another member of this series, namely UIrGe. This compound was found to exhibit antiferromagnetic ordering below 16 K /4/. As there is also some doubt whether these compounds form into the NiSiTi structure (space group: Pnma) the experiment was splitted into two parts: first to resolve the crystallographic structure and second to determine the nature of the ordered magnetic states. Therefore we collected data at 30 K, which is above the ordering temperature, and at 11 K. Concerning the crystallographic structure we were able to prove unambiguously, that UIrGe forms in the NiTiSi crystal structure. This structure accounts for the seven reflections (3,0,2), (3,1,1), (3,3,2), (5,0,2), (5,1,1), (5,2,2), and (6,1,0) indicated by arrows in figure 1. The refined Atomic positions were :</p> <table border="0"> <tr> <td>U</td> <td>x</td> <td>1/4</td> <td>z</td> <td>x = 0.00585;</td> <td>z = 0.20119</td> </tr> <tr> <td>Ir</td> <td>x</td> <td>1/4</td> <td>z</td> <td>x = 0.18567;</td> <td>z = 0.58606</td> </tr> <tr> <td>Ge</td> <td>x</td> <td>1/4</td> <td>z</td> <td>x = 0.77813;</td> <td>z = 0.58685</td> </tr> </table> <p>Concerning the magnetism the experiments were less successful. No additional peaks were found for the data taken at a nominal temperature of 11 K. As the ordering temperature of UIrGe is close to this temperature we can not exclude, that the temperature of the sample during this run was above the ordering temperature due to bad heat contact and/or poor</p>			U	x	1/4	z	x = 0.00585;	z = 0.20119	Ir	x	1/4	z	x = 0.18567;	z = 0.58606	Ge	x	1/4	z	x = 0.77813;	z = 0.58685
U	x	1/4	z	x = 0.00585;	z = 0.20119															
Ir	x	1/4	z	x = 0.18567;	z = 0.58606															
Ge	x	1/4	z	x = 0.77813;	z = 0.58685															

Experiment report (continued):

calibration of the thermometer. Therefore, we plan to repeat this experiment using a helium cryostat.

Figure 1: Portions of diffraction patterns from UIrGe taken at 30 K in one of the 153.4° banks of HIPD. The solid line in the upper plot represents the fit for the ordered crystal structure Pnma. Note that the space group Imma does not account for the reflections indicated by arrows.

References:

- /1/ V. Sechovsky and L. Havela, in *Ferromagn. Mater.* Vol.4 (1988), ed.: E.P. Wohlfarth and K.H.J. Buschow, p. 309
- /2/ R.A. Robinson et. al., submitted to *Phys. Rev. B* (1992)
- /3/ S. Kawamata et. al., *J.Magn.Magn.Mater.* (1991)
- /4/ E. Bruck, Ph. D. thesis, Amsterdam, 1991

Instrument used: <i>(please type)</i> HIPD	Local contact: Dr. R. Von Dreele Dr. T. Rieker	Proposal number: <i>(for LANSCE use only)</i> 5010
Title: Neutron Scattering Investigation of Non-ideal Behavior of Binary Liquid Mixtures Using Contrast Variation		Report received: <i>(for LANSCE use only)</i> 11/30/92
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;">Dr. G.C. Straty</div> <div style="width: 65%;"> NIST Thermophysics Division, 838.02 Boulder, CO 80303 </div> </div> <div style="display: flex; justify-content: space-between; margin-top: 20px;"> <div style="width: 30%;">Dr. H.J.M. Hanley</div> <div style="width: 65%;"> NIST Thermophysics Division, 838.02 Boulder, CO 80303 </div> </div>		
Experiment report: <p style="text-align: center;">The object of the experiments was to obtain information on the partial structure factors of molecular species in binary liquid mixtures in which the species differ in size and conformation. During our allotted time, however, technical problems with the beam limited the experiments to about 5 hours of reduced intensity beam on sample. These limited data were not sufficient for meaningful analysis.</p>		

Instrument used: <i>(please type)</i> HIPD	Local contact: Dr R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5035								
Title: Experimental Evaluation of Extinction and Absorption Theories for Neutron Time-of-Flight Diffraction.		Report received: <i>(for LANSCE use only)</i> 4 / 1 / 93								
Authors and affiliations: <table> <tr> <td>W. Kalceff</td> <td>Dept. of Applied Physics, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.</td> </tr> <tr> <td>T.M. Sabine</td> <td>Advanced Material Program, ANSTO, Private Mail Bag, Menai, NSW, Australia.</td> </tr> <tr> <td>J.P. Cline</td> <td>Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD 20899, USA.</td> </tr> <tr> <td>R.B. Von Dreele</td> <td>LANSCE MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.</td> </tr> </table>			W. Kalceff	Dept. of Applied Physics, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.	T.M. Sabine	Advanced Material Program, ANSTO, Private Mail Bag, Menai, NSW, Australia.	J.P. Cline	Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD 20899, USA.	R.B. Von Dreele	LANSCE MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.
W. Kalceff	Dept. of Applied Physics, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia.									
T.M. Sabine	Advanced Material Program, ANSTO, Private Mail Bag, Menai, NSW, Australia.									
J.P. Cline	Materials Science and Engineering Laboratory, NIST, Gaithersburg, MD 20899, USA.									
R.B. Von Dreele	LANSCE MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.									
Experiment report: <p>Three samples in each of three crystallite size ranges (0.2-0.5μm, 3-5μm and 10-20μm) were prepared having general stoichiometry (Ce_{1-x}Dy_x)O₂, with x (the Dy composition) taking values of 0, 0.05 and 0.1.</p> <p>These sample characteristics were chosen to facilitate the understanding of the simultaneous extinction and absorption effects active in the neutron scattering process: the varying particle sizes determine the degree of extinction, while absorption is controlled by the Dy composition.</p> <p>Nine HIPD runs were completed on the samples, averaging several hours per specimen. This was somewhat less than had been planned, but was necessitated by the loss of about 50% of the allocated time due to unscheduled outages.</p> <p>Analysis of the data has not yet been completed, with strong correlations between extinction, absorption and temperature factors contributing to the difficulty of its interpretation. A detailed electron microscopy study of the samples is in train in order to justify the constraint of various refinement parameters in the GSAS analysis.</p>										

Instrument used: <i>(please type)</i> HIPD	Local contact: Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5013
Title: Crystal structure of the 8.4Å kaolinite-hydrate complex		Report received: <i>(for LANSCE use only)</i> 1 / 15 / 93
Authors and affiliations: David L. Bish, Los Alamos National Laboratory, EES-1 Rossman F. Giese, Jr., Department of Geological Sciences, SUNY at Buffalo, Amherst, NY 14226 Patricia M. Costanzo, Earth Dimensions, Inc., 1091 Jamison Rd., Elma, NY 14059		
Experiment report: <p>Kaolinite, $\text{Al}_2\text{SiO}_5(\text{OH})_4$, is one of the most common and important clay minerals on the surface of the earth. The mineral has a layer structure in which the hydroxyl groups of one layer interact with the oxygen surface of the adjacent layer. Many of the properties of the mineral depend on the nature of the interlayer bonding, and there are several aspects of the interlayer bonding in kaolin minerals that are poorly understood. A naturally hydrated species of kaolinite, known as halloysite, exists in which water molecules occupy interlayer sites and result in an expanded c unit repeat. Unfortunately, this material is without fail very poorly crystalline, with poor layer stacking order so that no three-dimensional structural information is available for this phase. Recently, Costanzo et al. (1982; 1984) successfully synthesized a material resembling halloysite using a well-crystallized kaolinite as a starting material. The synthesized product has several stable hydration states, just as does halloysite. However, the synthetic material differs from halloysite in one crucial and unusual aspect; the 8.4Å complex exhibits very good three-dimensional order, yielding a diffraction pattern without appreciable two-dimensional diffraction effects and that is sufficiently resolved to allow the application of the Rietveld method. We recently determined the structure of the 8.4Å complex using X-ray powder diffraction data coupled with distance least-squares, Rietveld, and difference-Fourier methods (Bish et al., 1992). We were able to locate the position of the interlayer water(?) molecule but were unable to determine the orientation of the water molecule or if any of the inner-surface hydroxyl groups were replaced by the fluorine used in the synthesis process.</p> <p>Our powder neutron diffraction experiment was designed to determine the orientation of the interlayer water molecules and the possibility of substitution of F for OH. In addition, we intended to investigate the hydrogen bonding scheme from the interlayer water molecule to the kaolinite interlayer surface oxygens. This was the first ever attempt at refining the structure of a clay mineral with a hydrous interlayer component. Unfortunately, limited beam time and the large portion of H in this material resulted in data with a very poor peak to background ratio (Fig. 2). Data were obtained at room temperature using a small silica glass</p>		

Experiment report (*continued*):

capillary (<1 day collection time). To date, we have been unsuccessful in attempts to extract information from the very poor powder pattern. Refinements including the final positions from the X-ray refinement and modeled positions of most of the H atoms in the structure also were unsuccessful. In summary, our failure to perform a successful refinement is probably related to two factors: 1) poor quality data; and 2) a large amount of H is unaccounted for in the model structure, probably resulting in many incorrect phases.

Figure 1. Time-of-flight neutron diffraction pattern of kaolinite-hydrate

References:

- Bish, D. L., Giese, R. F., Jr., and Costanzo, P. M. (1992) Rietveld refinement of the crystal structure of the synthetic 8.4Å hydrated kaolinite complex. Proc. 29th Ann. Meeting of the Clay Min. Soc., Minneapolis, Minn.
- Costanzo, P. M., Giese, R. F., Lipsicas, M., and Straley, C. (1982) Synthesis of quasi-stable kaolinite and heat capacity of interlayer water. *Nature*, 296, 549-551.
- Costanzo, P. M., Giese, R. F., and Lipsicas, M. (1984) Static and dynamic structure of water in hydrated kaolinites: Part I. The static structure. *Clays & Clay Minerals*, 32, 419-428.

Instrument used: <i>(please type)</i> HIPD	Local contact: R. A. Robinson	Proposal number: <i>(for LANSCE use only)</i> 5037
Title: Pressure Dependence of Antiferromagnetic Moment in CeRh_2Si_2		Report received: <i>(for LANSCE use only)</i> 4/8/93
Authors and affiliations: R. A. Robinson, LANSCE, LANL P. C. Canfield, P-10, LANL J. D. Thompson, P-10, LANL A. Purwanto, New Mexico State University		
Experiment report: <p>The purpose of this proposal was to study the effect of applied pressure on an f-electron system in which hybridisation with conduction electrons is important. Ideally, we wanted to study UNiSn, in which the Néel temperature is raised by 10K on the application of 20kbar of hydrostatic pressure[1], in order to determine the effect on the moment. This turned out to be impossible from a bureaucratic point of view, so we decided to study CeRh_2Si_2[2] instead. In this case, the Néel temperature is depressed significantly on the application of pressure.</p> <p>1.5g of powdered sample was loaded into teflon cup, along with sodium chloride powder pressure calibrant and fluorinert pressure medium. This was in turn loaded into a Be-Cu clamp-type pressure cell, which was mounted on HIPD. The resultant signal, in one of the 90° banks is shown in Figure 1(a). For the sake of comparison, Figure 1(b) shows the same sample in a simple vanadium tube - the peaks in this pattern can all be indexed as from the published structures of CeRh_2Si_2[3] and NaCl. Clearly, the results in Fig. 1(a) are dominated by other scattering - the reflections around $2.0\text{\AA}$ are from the copper of the Be-Cu cell. At this point, we have not identified the origin of the reflection at $4.9\text{\AA}$. Clearly, before we attempt similar experiments again, we need to work on shielding the cell properly and on defining the incident and final collimations in an accurate and reproduceable way.</p> <p>Figure. Scattering into the $+90^\circ$ bank of HIPD (a) from CeRh_2Si_2 and NaCl in a Be-Cu pressure cell and (b) from CeRh_2Si_2 and NaCl in a vanadium can. Both measurements were at room temperature.</p>		

Experiment report (continued):

CERH2Si2 + NaCl IN BECU CELL, RT, AMBIENT PRESSURE
BANK NO. = 3 TWO-THETA = 90.00 OBSERVED PROFILE

CERH2Si2 AT RT
BANK NO. = 3 TWO-THETA = 90.00 OBSERVED PROFILE

References:

- [1] M. Kurisu, H. Kawanaka, T. Takabatake and H. Fujii, J. Phys. Soc. Japan 60, 3792 (1991).
- [2] J. D. Thompson, R. D. Parks and H. Borges, J. Magn. Magn. Mater. 54-57 (1986).
- [3] B. H. Grier, J. M. Lawrence, V. Murgai and R. D. Parks, Phys. Rev. B29, 2664 (1984).

Instrument Used: <i>(please type)</i> HIPD	Local Contact R. B. Von Dreele	Proposal Number: <i>(for LANSCE Use Only)</i> 5046
Title: Report on: "A New Approach to Neutron Texture Measurements: profile Analysis and Combination with Structure Refinements"		Report received: <i>(for LANSCE Use Only)</i> 1/21/93
Authors and affiliations: H.-R Wenk, Department Geology and Geophysics, U. C. Berkeley S. Matthies, Department Geology and Geophysics, U. C. Berkeley A. C. Larson, LANSCE R. B. Von Dreele, LANSCE J. A. Goldstone, LANSCE		
Experiment report <i>(continued)</i>: Report on: "A New Approach to Neutron Texture Measurements: profile Analysis and Combination with Structure Refinements" <p>In Fall 1991 a new concept of texture analysis by continuous profile analysis was proposed, analogous to the crystallographic Rietveld method. It had enthusiastic response. In January 1992 a detailed program was established with support from LANL for local system development (Von Dreele, HIPD and GSAS) and from UCB-NSF for development of new texture codes to be incorporated into GSAS. Professor S. Matthies visited Berkeley for 6 months to work on the project. Also we were awarded beam time on the HIPD.</p> <p>The specific plan was:</p> <ol style="list-style-type: none"> 1) Prepare a synthetic texture for tests with GSAS. 2) Use already measured ILL data to test newly developed software. 3) Measure a standard sample with the HIPD and analyze results. <p>The Berkeley team completed its software development and interacted with the LANSCE team during 3 visits. The results are the following:</p>		

Experiment report *(continued)*:

1) It was so far not possible to generate synthetic texture data with GSAS nor could texture information be extracted. Part of the problem were computer failures which coincided with our Los Alamos visits and the difficulties in modifying the complex GSAS package.

2) LANSCE was so far unable to read the ILL data tape which was provided in March 1992. Requests to return the tape to Berkeley for local processing have been so far ignored.

3) Three attempts (in July, August, and September) to measure a calcite standard sample according to a detailed measuring protocol prepared at Berkeley failed because of stepper motor problems.

We are still excited about this project and pursuing its implementation. While waiting for positive developments at LANSCE we are collaborating with Italian colleagues in Trento in implementing texture analysis into Rietveld codes and the calcite standard sample is presently being measured with TOF methods at Dubna. Results will be reported at the ICOTOM 93 meeting.

References:

Experiment report (continued):

References:

- [1] N.S. Boldrick and C.N.J. Wagner, IPNS Progress Report, 1986-1988, Argonne National Laboratory (1988) p. 4.
- [2] P. Ascarelli, Phys. Rev. 143, 36 (1966).

Instrument used: <i>(please type)</i> HIPD	Local contact: George Qwei	Proposal number: <i>(for LANSCE use only)</i> 5065
Title: Structural Characterization of $\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ by Neutron Powder Diffraction		Report received: <i>(for LANSCE use only)</i> 3/24/93
<p>Authors and affiliations:</p> <p>Fernando H. Garzon and Ian D. Raistrick MEE-11, MS D429 Los Alamos National Laboratory, Los Alamos, NM 87545 -----</p> <p>Eric L. Brosha and Peter K. Davies Department of Materials Science and Engineering University of Pennsylvania Philadelphia, Pa. 19104</p>		
<p>Experiment report:</p> <p>$\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ is a highly oxidized phase in the barium-copper oxide binary system. This phase has been reported in the literature (1) although determination of its apparently modulated structure has not been accomplished. Recently, it was shown that this is an extremely important phase in the Y-Ba-Cu-O system. (2, 3) Its presence dictates the low temperature stability of the high transition temperature superconducting compounds this system.</p> <p>We used a novel low-temperature synthesis technique utilizing the decomposition of ultrasonically prepared free-dried nitrate precursors to prepare bulk quantities of pure $\text{Ba}_2\text{Cu}_3\text{O}_6$ for x-ray and neutron powder diffraction studies. By utilizing this method, we also confirmed that this copper-rich barium cuprate close to the 2:3 ratio was a unique phase; several researchers have expressed doubts about its existence (4, 5). However, complete structure determination has been difficult.</p> <p>$\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ must be prepared at low temperatures when synthesis is carried out at 1 atmosphere oxygen partial pressure. Poor crystallinity and preferred orientation is common in low temperature solid-state synthesis. Structure determination is further complicated because of the peak broadening attributable to the sub micron particle sizes that are characteristic to the</p>		

Experiment report (continued):

ultrasonic process. (2) We feel that longer integration time would have been helpful in order to improve data especially in light of the significant beam down-time during this experiment.

Our current model for the $\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ structure is based on a NaCuO_2 -type structure.

(6) Previous studies using electron and x-ray diffraction (1) suggest that it is closely related to that of the trivalent cuprate, NaCuO_2 . This structure, in which infinite one-dimensional chains of edge-squared cuprate groups are linked by the larger electropositive cations, is adopted by several highly oxidized cuprates. For example, closely related ACuO_2 phases can be stabilized at low temperatures for $A=\text{K}$ (7), Cs (8), Rb (9). The same arrangement of cuprate chains is also found in the low-temperature form of calcium cuprate, $\text{Ca}_{1-x}\text{CuO}_2$ ($x=0.8-0.85$) (6) and in several ternary calcium-rare earth compounds, e.g. $(\text{Ca}_{2-x}\text{RE}_{2+x})\text{Cu}_5\text{O}_{10}$ ($\text{RE} = \text{Y}, \text{Gd}, \text{Nd}$) (10). The reduced occupancy of the larger inter-chain cation sites in these cation deficient compounds is accommodated by a modulation of the positions of the larger cations. It is these modulations, which can be commensurate or incommensurate, that have complicated the refinements of these compounds. The published models for $\text{Ba}_2\text{Cu}_3\text{O}_6$, or $\text{Ba}_{0.67}\text{CuO}_2$, indicate that this may be another example of a stable modulated NaCuO_2 -type structure. However, our theoretical neutron and x-ray diffraction patterns suggest that there are problems with the current model.

References:

- 1 J. G. Thompson et al., *Mat. Forum* **14**, 27-32 (1990).
- 2 E. L. Brosha et al., *Physica C* **184**, 353-361 (1991).
- 3 E.L. Brosha, F.H. Garzon, P.K. Davies, and I.D. Raistrick, in press, *Science* 1993.
- 4 M. Machida, K. Yasuoka, K. Eguchi, and H. Arai, *J. Solid State Chem.* **91**, 176-179 (1991).
- 5 S. Petricek, N. Bukovec, and P. Bukovec, *J. Solid State Chem.* **99**, 58-62 (1992).
- 6 T. Siegrist, R. S. Roth, C. J. Rawn, and J. J. Ritter, *Chem. Mat.* **2**, 192-194 (1990).
- 7 N. E. Brese et al., *J. Solid State Chem.* **83**, 1 (1989).
- 8 K. Wahl and W. Klemm, *Z. Anorg. Allg. Chem.* **270**, 69 (1952).
- 9 H. D. Wasel-Nielsen and R. Hoppe, *Z. Anorg. Allg. Chem.* **375**, 43 (1970).
- 10 P. K. Davies, *J. Solid State Chem.* **95**, 365-387 (1991).

Instrument Used: <i>(please type)</i> HIPD	Local Contact R. B. Von Dreele	Proposal Number: <i>(for LANSCE Use Only)</i> 5066
Title: Pair Distribution Function study of La ₂ -xBa _x CuO ₄		Report received: <i>(for LANSCE Use Only)</i> 2/22/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div> S.J.L. Billinge G.H. Kwei H. Takagi </div> <div> P10 P10 U. of Tokyo </div> </div>		
<p>Barium doped La₂CuO₄ undergoes a number of structural phase transitions as a function of temperature and doping, as well as exhibiting a superconducting transition. At high temperatures it is in the tetragonal K₂NiO₄ structure, often known as the high temperature tetragonal (HTT) structure. On cooling it transforms into a closely related structure which is in the orthorhombic space group Abma. This structure is often referred to as the low temperature orthorhombic structure (LTO). Finally, for compositions very close to x=0.125, where x denotes the barium level in the structure, the material undergoes a further transformation into another closely related phase, the low temperature tetragonal (LTT) phase. The properties of the material vary significantly between these phases, though the modification to the crystal structure are very small. Bulk superconductivity with high T_c's has been observed in the orthorhombic phase over the doping range approximately given by 0.1<x<0.2. On the other hand, the existence of superconductivity in the two tetragonal phases is less clear cut. In both cases, T_c's drop to low values and the superconducting fraction becomes very small. The effect is most marked in the LTT phase which exists at low temperature at a barium doping level which is close to the optimum doping level for the orthorhombic phase. It is clearly important to understand in what way such small modifications to the structure have such a large effect on the properties.</p> <p>Powder diffraction data from x=0.15 and x=0.125 composition samples, collected on HIPD, has been analysed using a joint pair distribution function (PDF) and Rietveld refinement procedure. The analysis is still going on, however, a number of things are clear from the initial analysis. The most striking thing is that the PDF of the sample barely changes with temperature, and there is virtually no signature in the PDF of the long range structural transitions that are evident in the Rietveld refinements. The PDF's from the x=0.125 sample are shown in the figure. According to the phase diagram for this material, the HTT to LTO transition should occur at around 200K and the LTO to LTT transition at around 70K. No large scale changes in the local structure are evident at either of these temperatures. In particular, it is clear that in the HTT phase the planes are not crystallographically flat, as is implied by the crystal structure, but are buckled in a manner that is very similar to the low temperature phases. They are always buckled; however, the existence of the long-range phase transition implies that the long range ordering of tilts of the octahedra changes with temperature. The analysis is continuing to extract more specific details of the local structure.</p>		

Experiment report (continued):

Figure. PDF's from a sample of $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$ as a function of temperature. Each temperature is offset by 50nm^{-3}

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5077
Title: Determination of Hafnium/Tantalum and Sulfur/Oxygen Occupancies in New Mixed Metal Sulfides		Report received: <i>(for LANSCE use only)</i> 2/23/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;">H.F. Franzen</div> <div style="width: 65%;">Ames Laboratory 333 Spedding Hall Ames, IA 50011</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 30%;">Greg Marking</div> <div style="width: 65%;">Ames Laboratory 334 Spedding Hall Ames, IA 50011</div> </div> <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 30%;">Victor Young</div> <div style="width: 65%;">Iowa State University 110 Gilman Hall Ames, IA 50011</div> </div>		
Experiment report: <p>Interpretation, using GSAS software, of the experimental data collected on the HIPD for proposal #5077 has been difficult but none-the-less, valuable results have been obtained.</p> <p>For the κ-phase samples in the systems Zr-Ta-S and Zr-Nb-S it can be concluded that the 6g octahedral sulfur sites are populated with mixtures of sulfur, oxygen, and vacancies.</p> <p>X-ray powder and single crystal refinements gave metal site occupancies in the Zr-Ta-S systems. Additionally, the 6g site was refined as partially occupied by sulfur. Sulfur scattering factors > oxygen scattering factors for X-rays.</p> <p>Refinement of the metal occupancies using neutron data gave results comparable to those obtained with X-ray data, however it was felt that Zr/Ta ratios obtained from X-ray single crystal experiments were more accurate. The metal occupancies were fixed accordingly. The 6g site was refined as partially occupied by oxygen. Oxygen scattering lengths > sulfur scattering lengths for neutrons. Three equations in three unknowns yield the occupancy of the 6g site. The 6g site occupancy for the Zr-Nb-S kappa phase was similarly obtained.</p> <p>In the $\text{Hf}_{10}\text{Ta}_3\text{S}_3$ system, the goal was to obtain metal site occupancies for the novel "stuffed" gamma brass structure. Occupancies less than zero or greater than one were not allowed. Once a suitable model was obtained, we were able to refine both U_{iso}'s and fractional populations. The resulting Hf/Ta occupancy ratios follow the same trends which we have obtained previously in X-ray single crystal data interpretations using bond orders, distances, and other ideas,⁽¹⁾ however the overall stoichiometry resulting from the neutron experiment is far too Ta rich.</p> <p>In the $\text{Hf}_{10}\text{TaNb}_2\text{S}_3$ system, there are two interesting phases, the "stuffed" gamma brass phase and a kappa phase. This system is complicated in that all three</p>		

Experiment report (continued):

metals can possibly be found on any one metal site. Presently, the results are not complete, but it is felt that the S/O/vacancy population of the 6g site in the kappa phase will be found as above and that the metal occupancies can also be refined using a combination of neutron and X-ray data and making use of the following facts. Ta and Nb have nearly identical neutron scattering lengths but dramatically different X-ray scattering factors. The opposite holds true for Hf and Ta although the difference is not so dramatic. A summary of results follows.

sample	wRp	Rp	phase wt. %	6g occupancies %
κ -Zr/Ta/S	4.77	3.23	85 (2)	S 65: O 18: vac 17
κ -Zr/Nb/S*	6.77	3.94	80 (1)	S 40: O 35: vac 26
Hf ₁₀ TaNb ₂ S ₃ *	5.71	4.14	γ 69 (1): κ 31	S 72: O 7: vac 21
γ -Hf ₁₀ Ta ₃ S ₃	5.38	3.81	94 (1)	----

* preliminary results Gamma Brass Site Occupancies % (Neutron Data)

	M1 x,x,x	M2 x,x,x	M3 x,0,0	M4 x,y,z
Hf ₁₀ Ta ₃ S ₃	Ta 100	Ta63(6):Hf37	Hf65(5):Ta35	Hf63(4):Ta37
Hf ₁₀ TaNb ₂ S ₃ *	Ta	Nb	Hf	Hf

The difficulties encountered in this experiment include the following: 1) The differences in scattering lengths for the metals is not large. 2) It was impossible to synthesize perfectly homogeneous samples of the required volume using our synthetic techniques. 3) The presence of minor phases (< 5 wt%) made a total Rietveld refinement of all phases impossible. 4) Sample preparation for X-ray diffraction experiments involved fine grinding of the sample which caused oxidation and/or decomposition of the sample relative to the same samples which were coarser ground for the neutron experiments. 5) Sulfur sites for which X-ray single crystal refinements indicate only 100% sulfur occupancy tend to refine as non-positive definite and/or > 100% occupied for both neutron and X-ray powder refinements. These parameters must be fixed at reasonable values.

References:

1. G.A. Marking and H.F. Franzen, J. Amer. Chem. Soc., submitted

Instrument Used: <i>(please type)</i> HIPD	Local Contact R. B. Von Dreele	Proposal Number: <i>(for LANSCE Use Only)</i> 5116
Title: Local Atomic Structure of solid Rb3C60		Report received: <i>(for LANSCE Use Only)</i> 2/18/93
Authors and affiliations: T. Egami U. of Pennsylvania S.J.L. Billinge P10, LANL G.H. Kwei P10, LANL J.E. Fischer U. of Pennsylvania		
Experiment report: Interest in solid C60 has intensified since it was discovered that it can be doped and becomes superconducting with high Tc's [1]. As with any new material, one of the most important things to determine is the crystal structure. The gross features of this were quickly established. In the undoped state C60 molecules pack, rather like hard spheres, into a close packed FCC structure [2]. The superconducting compounds with composition A3C60, (A=alkaline earth) have the same packing [3]. However, the neutron scattering pattern contains a large amount of diffuse scattering which is not analysed in a conventional Rietveld refinement. The origin of this diffuse scattering is orientational disorder of the balls which, unlike hard spheres, are not completely isotropic. One attractive way of analysing scattering which has a large diffuse component is to obtain the atomic pair distribution function (PDF), by fourier transforming the normalised sample scattering function. In this experiment we have carried out this kind of analysis on data from a superconducting sample of Rb3C60. The analysis is still in progress. Figure 1 shows the PDF obtained from data taken at 10K. The sharp peaks in the data at low-r originate from intra-ball atom pair correlations which are well defined in space. Beyond approximately 0.4 nm a contribution appears from atom-atom pairs in which the atoms originate on neighbouring balls. This contribution to the total PDF increases as r increases. Above 0.7 nm intensity in the function comes entirely from inter-ball correlations. Because of the orientational disorder of the balls, these peaks are somewhat broad and ill defined in the PDF. The same function obtained from pure C60 at low temperature has much more structure in the function G(r) indicating a larger degree of orientational order in the undoped material [3]. A detailed analysis is in progress to extract information about the nature of the orientational order.		

Experiment report (continued):

Figure 1. PDF of Rb_3C_{60} from data taken at 10K. The function plotted is $G(r)$.

References:

- [1] A.F. Hebard et. al. *Nature* **350** 600 (1991).
- [2] P. W. Stephens et. al. *Nature* **351** 632 (1991).
- [3] R. Hu et. al, *Phys. Rev. B* **45** 9517 (1992).

Instrument Used: <i>(please type)</i> HIPD	Local Contact Ed Ong	Proposal Number: <i>(for LANSCE Use Only)</i> 5129
Title: Structure of Calcium-Ammonia Solvation Complexes Within Titanium Disulfide		Report received: <i>(for LANSCE Use Only)</i> 4/5/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> E.W. Ong W.S. Glaunsinger J.A. Goldstone R.B. Von Dreele </div> <div style="width: 65%;"> LANSCE, LANL Dept. of Chemistry, Arizona State University LANSCE, LANL LANSCE, LANL </div> </div>		
Experiment report: <p>Titanium disulfide, a lamellar chemical compound that has empty spaces between its slabs, has been utilized as the cathode material for high-energy-density lithium batteries. Polar molecules and metals are intercalated between the slabs of titanium disulfide in these application. The intercalation is accompanied by oxidation of the metal and polar molecules, both as guests between the host slabs. The design of batteries requires detailed understanding about how the various chemical species in them interact on the atomic scale. The rate of charging or recharging for the battery can be limited by how fast the cations can be transported through the electrolyte and the electrodes. The number of charging cycles that a battery can withstand is strongly dependent on the strength of interactions between the cathode material and the guest species that are incorporated. Over wide concentration ranges lithium and the alkaline earth cations form complexes with ammonia within titanium disulfide, with fixed ratios of ammonia-to-cation. The formation of these complexes will effect the transport rate of the cations as well as their interactions with the host.</p> <p>The vibrational motions associated with alkaline earth-ammonia complexes intercalated into titanium disulfide have been intensively studied by our group in the last five years. Many experiments were performed using the FDS. Structural data is needed, for normal coordinate analysis, to rigorously assign the many peaks in the inelastic spectra to specific vibrational modes of the complex. The neutron powder diffraction pattern of a calcium-ammonia intercalate with the composition $(\text{ND}_3)_{0.04}[\text{Ca}^{2+}_{0.102}(\text{ND}_3)_{0.29}](\text{ND}_4^+)_{0.04}\text{TiS}_2\text{O}_{.24}^-$ was obtained using the HIPD, at 300 °K, during the 1992 run cycle. This compound was studied with the NPD during the 1990 run cycle, at 300 °K and 15 °K. Though the NPD possess high resolution, it is limited by not having low angle detector banks, which would allow the observation of d-spacings greater than four angstroms. As a result, none of the 00L lines were observed.</p> <p>Refinement of the compound's crystal structure using combined x-ray and neutron data sets, with the aid of GSAS is currently underway. The neutron data indicate that the compound does not adopt a three-layered rhombohedral structure as suggested by the x-ray data. The unit cell of the compound is more likely a primitive type with trigonal symmetry, with lattice parameters measuring: $a = 3.421 \text{ \AA}$ and $c = 26.17 \text{ \AA}$. The guest reside between the host slabs as monolayers, suggesting that the calcium-ammonia complexes in the compound is nearly planar. From the HIPD data, we can</p>		

Experiment report *(continued)*:

rule out the basal plane superlattice hypothesis mentioned in the previous experimental report.

XAFS experiments at Stanford will begin in May 1993, to probe the local environment of the calcium cation in the complex, to supplement the neutron and x-ray data.

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: R. B. VON DREELE	Proposal number: <i>(for LANSCE use only)</i> 5133
Title: CRYSTAL AND MAGNETIC STRUCTURES OF $\text{LiMnXO}_4(\text{OD})$, MnAsO_4 and LiMnXO_4 (X=P, As)		Report received: <i>(for LANSCE use only)</i> 1/15/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>Dr. Miguel A. G. Aranda</p> <p>Prof. Sebastian Bruque</p> <p>Dr. Paul Attfield</p> </div> <div style="width: 50%;"> <p>Dept. Química Inorganica, Universidad de Málaga, Aptdo 59, 29071 - MALAGA</p> <p>SPAIN</p> <p>Department of Chemistry, University of Cambridge, CAMBRIDGE CB2 1EW</p> <p>UNITED KINGDOM</p> </div> </div>		
Experiment report: Crystal and Magnetic Structures of $\text{LiMn}^{\text{III}}\text{XO}_4(\text{OD})$ (X=P, As), and $\text{Mn}^{\text{III}}\text{AsO}_4$ <p>In the three days of beam time (four to six of September 1992), in the neutron powder diffractometer HIPD, we could obtained the diffraction data of three samples: $\text{LiMnAsO}_4(\text{OD})$, $\text{LiMnPO}_4(\text{OD})$, and MnAsO_4. These data were collected at room temperature and below the magnetic ordering temperature. The room temperature powder neutron diffraction data were used to refine the crystal structure (partially known from previous laboratory X-ray powder data) and to locate the deuterium/hydrogen position in the hydroxo compounds. The low temperature data has been used to refine the crystal structure and to resolve the magnetic structure. The ability to fit the low detector angle data (40°), needed to access the high d-spacing magnetic peaks, and the better resolved profiles from the 90° and 150° detectors simultaneously, has given a precise refinement of both nuclear and magnetic structures. The data processing has been carried out by using the GSAS program.</p> <p>$\text{LiMnAsO}_4(\text{OD})$</p> <p>a) The Rietveld refinement of the room temperature powder neutron data reveals that the framework of this compound determined using X-ray laboratory powder diffraction data was correct. The more outstanding results of this refinement were the confirmation of the lithium position into the channels and the determination of the deuterium/hydrogen position via a difference of Fourier map. The refined D/H ratio was 59.9(3)% of D. The D/H are also located into the channels, and the geometry of the non-linear hydrogen bond has been obtained: $\text{O}(3) - \text{D}/\text{H} 0.976(5) \text{ \AA}$, $\text{O}(2a) \cdots \text{D}/\text{H} 1.827(6) \text{ \AA}$, and $\text{O}(2a) \cdots \text{D}/\text{H} \cdots \text{O}(3) 164.0(5)^\circ$.</p> <p>b) From the 10 K powder neutron diffraction data, the magnetic structure of this compound has been resolved. Magnetics peaks were cleared observed, and could be indexed in the initial C-centered triclinic unit cell. The two crystallographic independent manganese atoms lie in a special position and the better refinement was achieved for the following configuration of Mn spins: $\text{Mn}(a) (1/4, 1/4, 0) +$; $\text{Mn}(a) (3/4, 3/4, 0) -$; $\text{Mn}(b) (3/4, 1/4, 1/2) +$; $\text{Mn}(b) (1/4, 3/4, 1/2) -$. For the Mn at $(1/4, 1/4, 0)$ the refined components of the magnetic moments were $M_x = 0.82(4)$, $M_y = 3.28(5)$ and $M_z = 0.79(6) \mu_B$. Resulting in a total magnetic moment of $3.47(5) \mu_B$. The magnetic structure consists of infinite chains $-\text{Mn}(a)-\text{O}(3)-\text{Mn}(b)-$ coupled ferromagnetically, being these chains coupled antiferromagnetically. The Rietveld plot of the high d-spacing data is shown in Figure 1a.</p>		

Experiment report (continued):

LiMnPO₄(OD)

a) The lithium position has also been confirmed, and the deuterium/hydrogen position located via a difference of Fourier map. The refined D/H ratio has been 44.2(2)% of D. The geometry of the non-linear hydrogen bond is: O(3) - D/H 1.06(1) Å, O(1b) ... D/H 1.67(1) Å, and O(1b) ... D/H ... O(3) 166(1) °.

b) Magnetics peaks were clearly observed in the 10 K powder neutron diffraction data. These peaks could be indexed in the original C-centered triclinic unit cell. The two crystallographic independent manganese atoms lie in a special position and the better refinement was achieved for the following configuration of Mn spins: Mn(a) (0,0,0) +; Mn(a) (1/2,1/2,0) -; Mn(b) (0,0,1/2) +; Mn(b) (1/2,1/2,1/2) -. For the Mn at (0,0,0) the refined components of the magnetic moments were $M_x = 0.64(3)$, $M_y = 3.38(6)$ and $M_z = -0.44(5) \mu_B$. Resulting in a total magnetic moment of $3.46(5) \mu_B$. The magnetic structure consists of infinite chains -Mn(a)-O(3)-Mn(b)- coupled ferromagnetically, being these chains coupled antiferromagnetically. The Rietveld plot of the high d-spacing data is shown in Figure 1b.

MnAsO₄

The low temperature pattern (10 K) presents magnetics peaks. These peaks can be indexed in the doubled monoclinic unit cell. The data analysis is still in progress.

Figure 1. Final observed (points), calculated (full line) and difference time-of-flight neutron diffraction patterns at 10 K from -40 ° detector for LiMnAsO₄(OD) (a), and for LiMnPO₄(OD) (b).

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5146						
Title: The Equation of State of Boron.		Report received: <i>(for LANSCE use only)</i> 4/16/93						
Authors and affiliations: <table border="0" style="width: 100%;"> <tr> <td style="vertical-align: top; width: 40%;"> R.J.Nelmes J.S.Loveday R.M.Wilson </td> <td style="vertical-align: top; width: 60%;"> Department of Physics The University of Edinburgh Edinburgh </td> </tr> <tr> <td style="vertical-align: top;"> J.M.Besson S.Klotz G.Hamel </td> <td style="vertical-align: top;"> Physique des Milieux Condensés (CNRS URA 782) Université Pierre et Marie Curie, Paris Département des Hautes Pressions Université Pierre et Marie Curie, Paris </td> </tr> <tr> <td style="vertical-align: top;"> R.B. von Dreele </td> <td style="vertical-align: top;"> LANSCE </td> </tr> </table>			R.J.Nelmes J.S.Loveday R.M.Wilson	Department of Physics The University of Edinburgh Edinburgh	J.M.Besson S.Klotz G.Hamel	Physique des Milieux Condensés (CNRS URA 782) Université Pierre et Marie Curie, Paris Département des Hautes Pressions Université Pierre et Marie Curie, Paris	R.B. von Dreele	LANSCE
R.J.Nelmes J.S.Loveday R.M.Wilson	Department of Physics The University of Edinburgh Edinburgh							
J.M.Besson S.Klotz G.Hamel	Physique des Milieux Condensés (CNRS URA 782) Université Pierre et Marie Curie, Paris Département des Hautes Pressions Université Pierre et Marie Curie, Paris							
R.B. von Dreele	LANSCE							
Experiment report: <p>Boron and some boron-rich compounds form a structurally unique class of materials. In all cases the common structural unit is an icosahedron in which each boron atom is five-fold co-ordinated. Boron has only three electrons available for bonding and so, with five nearest neighbours, it is not possible to form conventional covalent bonds. Instead bonding is thought to be achieved by an accumulation of charge at the centre of a triangle formed by three adjacent atoms leading to the formation of so-called three-centre electron-deficient bonds.</p> <p>Boron is rare amongst the common elements in that very little high-pressure work on it has been reported. In particular, the only static measurement of the bulk modulus until recently was that of Bridgman in 1930 [1].</p> <p>We have performed high-pressure neutron diffraction studies [2] on β-boron (a rhombohedral phase with 105 atoms/unit cell) which determined the value of the average bulk modulus (B) in the range 0-9 GPa to be 185(7) GPa. Though this value is large, it is significantly smaller than in other comparably hard materials such as diamond and cubic boron nitride, in accord with the notion of relatively weak bonding.</p> <p>Because of the complexity of the β-boron structure and its stiffness, it was not possible to determine the value of the pressure derivative of the bulk modulus, B'. The value of B' is considered to be indicative of the bonding type and our studies of other icosahedral boron-rich materials suggest that B' is smaller than found in normal covalent materials. Hence it was decided to repeat the measurements to obtain a more precise equation-of-state.</p> <p>The experiments were carried out at LANSCE using a pressure cell of our own design (the Paris-Edinburgh cell), on HIPD. Samples of ^{11}B-enriched β-boron were loaded into the cell along with NaCl as a pressure calibrant and a pressure transmitting medium (fluorinert). Spectra were collected from two loadings of the cell at pressures of up to 6 GPa for the first loading and 11 GPa for the second. Counting times varied between 12 hours at low pressures and 24 hours at the highest pressure.</p>								

Experiment report (continued):

The spectra were analysed by Rietveld profile analysis using GSAS. The values of the unit-cell volumes, corrected for the deformation of the pressure cell under load, are shown as a function of pressure in Figure 1, along with a best-fit Murnaghan equation-of-state which gave values for the bulk modulus and its derivative of $B_0 = 192(15)$ GPa and $B' = 0(4)$. These values are in good agreement with our earlier work for B_0 and provide the first determination of B' for any boron-rich material. The result obtained for B' suggests that it is probably less than the 'normal' value of 4 for covalent bonding. Further work to > 15 GPa is now planned to improve the precision.

Figure 1: The pressure dependence of the unit-cell volume of β -boron. The values shown as open triangles represent previous work while those shown as solid triangles represent values obtained from data collected at LANSCE. The solid line represents the best-fit Murnaghan equation-of-state.

References:

- [1] P.W. Bridgman. Proc. Am. Acad. Arts Sci **64**, 75 (1930).
- [2] R.J. Nelmes, J.S. Loveday, J.M. Besson, G. Hamel, P. Grima and S. Hull, Phys. Rev. **B47** (1993) in press.

Instrument used: <i>(please type)</i> HIPD	Local contact: A. C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 5405
Title: Debye-Waller Factors of α-Plutonium		Report received: <i>(for LANSCE use only)</i> 3/10/93
Authors and affiliations: <p style="text-align: center;">A. C. Lawson, J. A. Goldstone, B. Cort and R. B. Von Dreele Los Alamos National Laboratory Los Alamos, NM 87545</p>		
Experiment report: <p>During 1992 we repeated our determination of the Debye-Waller factors of α-plutonium. The previous experiment[1] had suffered somewhat from lack of usable beam and consequent poor temperature control. The present experiment was a complete technical success, and we obtained data at nine temperature between 15 and 310K.</p> <p>In view of previous findings that the "offset" term arising in the analysis of Debye-Waller data depends on the number of background terms and that the Debye temperature (theta) shows and interesting temperature dependence, we decided to make a thorough analysis of the effect of the background function on the data analysis. The figure shows a plot of $\langle u^2 \rangle$ versus temperature for each of three different background functions (solid symbols). Two of the curves are for the GSAS standard background functions, the Chebychev (dashed line) and the Fourier (dotted line). The discrepancy between the results obtained with the use of these functions is quite unsatisfactory. However, its source was easy to discover and is shown in the upper part of the figure (open symbols): the background terms are themselves highly temperature dependent, and this dependence affects the refined thermal factors.</p> <p>The cure for this problem is a background function that correctly models the physics of the background scattering. We are now using a power series in the magnitude of the Q-vector:</p> $BG = B_1 + B_2 Q^2/2! + B_3 Q^4/4! + b_4 Q^6/6! + \dots$ <p>This is the correct asymptotic expansion of the thermal diffuse background scattering:</p> $B(t) = (d\sigma/d\Omega)_{inc} + (d\sigma/d\Omega)_{coh} [1 - \exp(-2 B \sin^2\theta / \lambda^2)]$ <p>as given in Windsor's monograph[2]. (The "B" on the right-hand side of this equation is the thermal factor.) This background should be only slightly temperature dependent through the contributions of the sample and its encapsulation.</p> <p>The temperature dependencies of this background function and of the resulting thermal factors are also shown in the figure (solid lines). As expected, the background is temperature independent. For clarity, we have shown only the first, constant, background term, b_1. The temperature behavior of the higher terms is similar for subsequent terms.</p> <p>It seems to be dangerous to use the older, somewhat arbitrary, background functions in GSAS for the analysis of temperature dependence of Debye-Waller factors. When we use the Q^2 function, we get as reasonable (but different) value for the Debye temperature with only a slight (but still interesting) temperature dependence.</p>		

Experiment report (continued):

References:

- [1] A. C. Lawson, J. A. Goldstone, B. Cort and L. Diebolt, "Debye-Waller Factors of α -Plutonium," LANSCE Experiment Reports, 1991 Run Cycle, submitted.
- [2] C. G. Windsor, Pulsed Neutron Scattering (London, Taylor and Francis Ltd., 1981) p. 294.

92 1144

*Neutron Powder
Diffractometer (NPD)*

Neutron Powder Diffractometer (NPD)

The sample position for the Neutron Powder Diffractometer (NPD) is 32 m from the source. Standard collimation in the beam line produces a 5.0×1.0 cm beam at the sample position. Placed at five points along the beam, variable apertures permit adjustment of both the beam size on the sample and the viewed region of the moderator. The large evacuated sample can (74 cm inside diameter) has sufficient clearance to handle any special environment device necessary. Detectors are placed symmetrically at several angles to cover short d-spacings (0.25 to 3.9 Å) at a resolution ($\Delta d/d=0.15\%$) to much longer d-spacings (~ 34 Å) at lower resolution ($\Delta d/d=0.5-1.5\%$). Both sides of the instrument have identical resolution because the incident beam is normal to the moderator. The resolution of the instrument can be adjusted by changing the collimation and the detector-position resolution.

Instrument Details

Detector banks:	$\pm 20^\circ$ (future) $\pm 45^\circ$ (future) $\pm 90^\circ$ $\pm 148^\circ$
d-spacing range for 12- Hz operation (approximate):	$\pm 20^\circ$ 1.2 - 33.6 Å $\pm 45^\circ$ 0.65 - 12.7 Å $\pm 90^\circ$ 0.35 - 7.8 Å $\pm 148^\circ$ 0.25 - 5.2 Å
Resolution (determined by collimation):	$\pm 20^\circ$ 0.91 - 1.5% $\pm 45^\circ$ 0.37 - 0.62% $\pm 90^\circ$ 0.25% $\pm 148^\circ$ 0.15%
Moderator	Chilled water at 10° C
Sample environment	10 - 300 K, closed cycle refrigerator; room-temperature-access liquid-He dewar, 1.2 - 300 K; vacuum furnace, limit 700° C Manipulation and Collimation System
Maximum beam size at sample:	5 cm (height) x 1 cm diameter
Experiment duration	8 - 48 hours

Joyce Goldstone, instrument scientist
John Thomas, instrument technician

NPD Experiment reports

5000	<i>Crystal Structures of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ Phases</i>	54
5002	<i>UPdSn: Is there an Orthorhombic Distortion below the Néel Point?</i>	56
5012	<i>Cation Order and Oxygen Nonstoichiometry in Perovskite Oxides Containing Pb, Sb, and Bi</i>	58
5012.1	<i>Low-Temperature Crystal Structure of ZnV_2O_4</i>	60
5059	<i>Stress and Strain Incompatibility in a Cu-15 vol.% Nb Composite</i>	62
5069	<i>Measurement of Interface Residual Strains at Reaction Bonded Interfaces</i>	64
5074	<i>Phase Identification of Shock-Loaded Deuterated Ice</i>	66
5075	<i>Texture Measurement of Experimentally Deformed High-Pressure Low-Temperature D_2O Ice</i>	68
5092	<i>To Determine the Structure of $\text{Pr}_{11}\text{O}_{20}$</i>	70
5098	<i>Rietveld Structure Refinement of Diffuse Phase Transition Ferroelectrics</i>	72
5122	<i>In Situ Strain Measurement in AlTiC Composite During Loading</i>	74
5153	<i>Structural Changes Accompanying Heating of the RHO-Framework: High Temperature Study of Tl-Exchanged BePO-RHO</i>	76
5169	<i>A Neutron and X-ray Diffraction Study of $\text{Ni}_{0.82}\text{Cu}_{0.18}\text{Cr}_2\text{O}_4$ and $\text{Ni}_{0.18}\text{Cu}_{0.82}\text{Cr}_2\text{O}_4$</i>	78
5400	<i>Thermal Expansion of $\eta\text{-Pu}_{0.90}\text{Np}_{0.10}$</i>	80
5701	<i>Residual Strain Measurement in a Ti 24 11 SCS6 08 MMC</i>	82

Instrument used: (please type) NPD	Local contact: Joyce Goldstone	Proposal number: (for LANSCE use only) 5000
Title: Crystal Structures of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ Phases		Report received: (for LANSCE use only) 2/22/93
<p>Authors and affiliations:</p> <p>William T. A. Harrison,* Allan J. Jacobson,* Ingrid J. Pickering,¶ and Joseph T. Lewandowski.¶</p> <p>*Department of Chemistry, University of Houston, Houston, TX 77204-5641; ¶Corporate Research, Exxon Research and Engineering Company, Route 22 E, Annandale, NJ 08801.</p>		
<p>Experiment report:</p> <p>Lithium nickel oxide has found application in molten carbonate fuel cell, electrochemical cells and methane oxidative-coupling catalysis. The solid solution $\text{Li}_x\text{Ni}_{1-x}\text{O}$ exists over the complete solid-solution range $0 < x < 0.5$. All compositions have structures derived from cubic rock salt, but a rhombohedral distortion, indicative of Li^+ ordering on alternate $\langle 111 \rangle$ planes, occurs for $x > 0.3$.¹</p> <p>Despite the many previous studies on this system, detailed information concerning the Li/Ni and $\text{Ni}^{2+}/\text{Ni}^{3+}$ cation distributions within the rhombohedral layers is lacking. Therefore, the structures of three samples of $\text{Li}_x\text{Ni}_{1-x}\text{O}$ ($x = 0.3, 0.32, 0.48$) were examined using the Neutron Powder Diffractometer (NPD) at LANSCE.</p> <p>Excellent quality data were accumulated in a few hours of $\sim 70 \mu\text{A}$ beam time, for each sample. The rhombohedral distortion mode was confirmed, and Rietveld profile analysis was carried out using the program GSAS.² Excellent agreement (e.g., Figures 1 & 2) was attained for each sample. We are now carrying out detailed analysis of the cation distributions within the layers and relating these distributions to the catalytic and other properties of these materials.</p>		

Experiment report (continued):

Li_{0.32}Ni_{0.68}O

Li_{0.48}Ni_{0.52}O

References:

- (1) I. J. Pickering, J. T. Lewandowski, A. J. Jacobson and J. A. Goldstone, *Sol. St. Ionics* 1992, **53-56**, 405.
- (2) A. C. Larson and R. B. Von Dreele, *GSAS User Guide*, Los Alamos National Laboratory, 1990.

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
NPD	A. C. Lawson	5002
Title: UPdSn: Is there an orthorhombic distortion below the Néel point?		Report received: <i>(for LANSCE use only)</i> 11/30/92
Authors and affiliations: <p>R. A. Robinson, LANSCE, LANL A. C. Lawson, MST Division, LANL J. A. Goldstone, LANSCE, LANL K. H. J. Buschow, Philips Research Labs., Eindhoven</p>		
Experiment report: <p>The intermetallic compound UPdSn has been studied by means of high-resolution neutron powder diffraction at low temperature and both orthorhombic and monoclinic structural distortions have been observed. The 110 hexagonal reflection is most sensitive to this effect and it is shown at various temperatures in Fig. 1. In addition to confirming the previously published noncollinear antiferromagnetic structures with these symmetries[1], full joint Rietveld refinements including the magnetic cross sections have been made on the new data, together with older low-resolution data taken on HIPD. The picture that emerges is of a monoclinic phase below 25K with space group $P2_1$ and magnetic symmetry P_c2_1, an orthorhombic phase between 25K and 40K with space group $Cmc2_1$ and magnetic symmetry P_Cmc2_1, and a paramagnetic hexagonal phase above 40K with space group $P6_3mc$. The temperature variations of the orthorhombicity $(b/\sqrt{3} - a)$ and monoclinicity $(90-\gamma)$ parameters have been extracted (see Fig. 2) and the monoclinicity is linearly coupled to the x-component of the uranium magnetic moment, the "magnetic monoclinicity" order parameter. In contrast, the orthorhombicity seems to be coupled to the total uranium magnetic moment. It has also been possible to determine the sign of the coupling between μ_x and $90-\gamma$. It is positive, that is the projected moments prefer to point across the shorter diagonal of the monoclinic basal plane, rather than the longer diagonal. The resultant structure is shown schematically in Fig. 3</p> <p>This work has been submitted for publication[2].</p>		

Experiment report (continued):

Fig. 1

Fig. 2

Fig. 3

References:

- [1] R. A. Robinson, A. C. Lawson, K. H. J. Buschow, F. R. de Boer, V. Sechovsky and R. B. Von Dreele, *J. Magn. Magn. Mater.* 98, 147 (1991).
- [2] R. A. Robinson, A. C. Lawson, J. A. Goldstone and K. H. J. Buschow, submitted to *Phys. Rev. B* (1992).

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
Neutron Powder Diffractometer	Joyce Goldstone	5012
Title: Cation Order and Oxygen Nonstoichiometry in Perovskite Oxides Containing Pb, Sb and Bi.		Report received: <i>(for LANSCE use only)</i>
2/19/93		
Authors and affiliations: Allan J. Jacobson and Kenneth P. Reis Department of Chemistry, University of Houston, Houston, TX 77204-5641		
Experiment report: <p>The structures and cation ordering of three barium bismuth oxide phases, $\text{Ba}_{2+x}\text{Bi}_{2-x}\text{O}_{6-y}$ [$x = 0.22, 0.28, 0.4$], have been determined at ambient temperature from time-of-flight neutron powder diffraction data collected on NPD. The end member of this series $\text{Ba}_2\text{Bi(III)Bi(V)O}_6$, has a monoclinic distortion of the simple cubic perovskite structure with an ordered arrangement of the Bi^{3+} and Bi^{5+} cations on the B sites. The monoclinic structure at $x = 0$ changes first to a rhombohedral structure and then to cubic as some bismuth atoms are replaced by barium atoms. The change in symmetry is shown in Figure 1 for the pseudocubic 440 reflection which splits into $\bar{2}02$ and 422 in the primitive rhombohedral cell. At $x = 0.22$ the splitting is clearly visible but at $x = 0.28$ is apparent only in line broadening. The rhombohedral cell constants refine to $a = 6.1573\text{\AA}$, $\alpha = 60.247^\circ$ for $x = 0.22$ and $a = 6.1717\text{\AA}$, $\alpha = 60.136^\circ$ for $x = 0.28$. No departure from cubic symmetry is observed for the $x = 0.40$ composition. The data for the rhombohedral phases were refined using the GSAS programs [1] in space group $R\bar{3}$ and the cubic phase in $\text{Fm}\bar{3}\text{m}$ with a model based on 1:1 ordering of the B site cations, $\text{A}_2\text{BB}'\text{O}_6$ [2]. The results show that when the additional barium atoms are introduced into the structure, substitution of Ba for Bi(III) occurs to give phases with the general composition $\text{Ba}_2[(\text{Bi}_{1-x}\text{Ba}_x)\text{Bi}]\text{O}_6$. The replacement of Bi(III) by Ba^{2+} on one of the B sites, however, introduces considerable disorder into the structure which is reflected in large apparent thermal parameters for all of the atoms but especially the oxygen atoms. The disorder limits the degree of detailed bond distance information which can be obtained. The quality of the fits to the data also decrease somewhat as the barium content increases. The data for the $x = 0.22$ phase is shown in Figure 2. In addition to the Ba/Bi phases, the structure of $\text{Ba}_4\text{Sb}_3\text{NaO}_{12}$ has also been refined in space group $\text{Im}\bar{3}\text{m}$ with $a = 8.273(4)\text{\AA}$ [3].</p>		

Experiment report (continued):

Figure 1. Neutron diffraction data for the cubic (440) of $\text{Ba}_{2+x}\text{Bi}_{2-x}\text{O}_{6-y}$ at $x = 0.22, 0.28, 0.40$.

Figure 2. Time-of-flight neutron diffraction data for $\text{Ba}_2[\text{Ba}_{0.22}\text{Bi}_{0.78}]\text{BiO}_6$

References:

- [1] General Structure Analysis System, A. C. Larson and R. B. Von Dreele, LANSCE, MS-H805, Los Alamos National Laboratory, Los Alamos, NM 87545.
- [2] K. P. Reis, A. J. Jacobson and J. M. Nicol, Journal of Solid State Chemistry submitted.
- [3] K. Reis and A. J. Jacobson, Acta Cryst C submitted.

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce Goldstone	Proposal number: <i>(for LANSCE use only)</i> 5012.1
Title: Low-Temperature Crystal Structure of ZnV_2O_4		Report received: <i>(for LANSCE use only)</i> 3/10/93
<p>Authors and affiliations:</p> <p>William T. A. Harrison,* Allan J. Jacobson,* Konrad Bussmann§ and John. B. Goodenough.§</p> <p><i>*Department of Chemistry, University of Houston, Houston, TX 77204-5641; §Department of Materials Science and Engineering, University of Texas, Austin, TX.</i></p>		
<p>Experiment report:</p> <p>The spinel-type phase zinc vanadium oxide, ZnV_2O_4 is Mott-Hubbard insulator, having a partially-filled <i>d</i>-band which shows a metal-insulator transition and Curie-Weiss magnetic behavior.¹ However, the detailed low-temperature crystal structure and magnetic-ordering pattern are not known. Low-temperature (15 K) neutron diffraction data for ZnV_2O_4 were collected over a 6-hour period (typical beam current = 70 μA), using the Neutron Powder Diffractometer (NPD) at LANSCE. Data analysis was carried out using the program GSAS.²</p> <p>All the observed diffraction peaks could be indexed on a body-centered tetragonal unit cell, with $a = 5.95026(6) \text{ \AA}$ and $c = 8.36971(10) \text{ \AA}$. The refinement (Figure 1) progressed very smoothly in space group $I4_1/amd$ (No. 141), which is a "well-behaved" symmetry-lowering transition from the room-temperature $Fd\bar{3}m$ structure. Other distorted spinels such as ZnMn_2O_4 and NiRh_2O_4 show similar behavior.</p> <p>The most significant structural change involves the environment of the vanadium atom lowering from $\bar{3}m$ (cubic) to $.2/m.$ (tetragonal) site-symmetry, and slight shortening of two of the six V-O bonds. There was no evidence for any coherent magnetic neutron diffraction peaks, perhaps because the neutron flux is weak at the long <i>d</i>-spacings where such peaks might be observed. However, the low-temperature tetragonal symmetry has been quite unambiguously established.</p>		

Experiment report (continued):

Figure 1: Rietveld profiles for ZnV₂O₄ (+148° detector bank).

References:

- (1) S. Nizol, *Phys. Stat. Sol.* 1973, **18**, K11.
- (2) A. C. Larson and R. B. Von Dreele, *GSAS User Guide*, Los Alamos National Laboratory, 1990.

Instrument used: <i>(please type)</i> NPD	Local contact: J.A. Goldstone	Proposal number: <i>(for LANSCE use only)</i> 5059
Title: STRESS AND STRAIN INCOMPATIBILITY IN A CU-15 vol.% Nb COMPOSITE		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations:		
G.T. Gray III	MST-5, MS G730	LANL
M. Bourke	LANSCE, MS H805	LANL
A.C. Lawson	MST-5, MS G730	LANL
J.A. Goldstone	LANSCE, MS H805	LANL
Experiment report:		
<p>Alloys containing two insoluble ductile phases can be heavily cold worked by rolling or swaging resulting in in-situ composites, termed HDISC for heavily deformed in-situ composites, with microstructural morphologies similar to those found in conventional lamellar or fibrous composites[1-4]. Mechanical property studies have revealed that these composites often exceed that predicted on a "rule-of mixtures" basis which takes into account strengthening produced by the cold working of the individual phases. In addition, the work-hardening rates of HDISC do not decrease as processing strain increases. This behavior is drastically different from that of single-phase alloys and alloys strengthened with non-deforming second phases or dispersoids. Large-strain deformation of HDISC is accompanied by appreciable increases in the interphase boundary area per unit volume and dislocation density[3]. A chief cause of this high defect density is the inherent strain incompatibility between phases. In addition, due to the over a factor of two difference in the thermal expansion coefficient between copper and niobium, these alloys in an annealed and quenched condition contain residual stresses prior to deformation. Understanding of the strength and hardening behavior of HDISC require a knowledge of the residual stresses and strains within each phase as a function of loading rate and temperature.</p> <p>The strain distribution in the Cu-Nb alloy as a function of pre-straining history was evaluated using the NPD facility at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. Diffraction data were obtained with specimens(nominally 10mm in dia. by 13mm in length)with the sample entirely within the beam. The compression axis of the sample was oriented 45° relative to the beam allowing simultaneous measurement of the transverse and longitudinal orientations for both the copper and niobium constituents using the ±90 degree banks. The specific purpose of this experiment was to determine: 1) the bulk residual stresses in a Cu-15 vol.% Nb composite in the as-rolled and annealed conditions, and 2) the relative strains in the copper and niobium phases as a function of deformation history. In particular, the strain distribution was evaluated following quasi-static and high-strain rate deformation at 298 K and 77K for the annealed material.</p> <p>Comparison of the microstrains in the niobium and matrix-copper revealed three significant observations. Firstly, consistent with the highly rolled condition of the starting plate material, parallel to the stress axis the niobium is initially quite significantly in compression (microstrains of 2000 to 3400) while the copper is slightly in tension (microstrains of 0 to 400). (Figures 1 and</p>		

Experiment report (continued):

2) The sense of the initial strain values was seen to be relatively similar for the data reduction using a range of plane reflections for the niobium and copper although some anisotropy is apparent. Secondly, the magnitude of the residual strain values in the niobium was found to increase with increasing severity of pre-straining, i.e., either decreasing temperature during quasi-static deformation or with increasing strain rate. High-strain-rate pre-straining at cryogenic temperature displayed the highest residual strains. These findings are consistent with the known deformation response of BCC metals. Due to the large lattice friction (Peierl's Stress) in niobium, as in other BCC metals particularly refractory metals, increasing strain rate or decreasing temperature will lead to a significantly higher flow stress in the niobium phase. Accordingly, the increased flow stress in the niobium under the high-rate or low-temperature deformation will lead to increased residual strains in the niobium phase. Micro-mechanical modeling of this composite system will endeavor to combine composite constitutive response with the residual strain data from this study to form a detailed composite description.

Figure 1: Axial Strain in the Niobium phase as a function of the sample pre-straining conditions.

Figure 2: Axial strain in the copper phase as a function of the sample pre-straining conditions.

References:

1. W.A. Spitzig and P.D. Krotz, Acta Metall., 36, 1988, pp. 1709-1715.
2. W.A. Spitzig, A.R. Pelton, and F.C. Laabs, Acta Metall., 35, 1987, pp. 2427-2442.
3. P.D. Funkenbusch, J.K. Lee, and T.H. Courtney, Metall. Trans., 18A, 1987, pp. 1249-1256.
4. P.D. Krotz, W.A. Spitzig, and F.C. Laabs, Mat. Sci. and Eng., A110, 1989, pp. 37-47.

Experiment report (continued):

seven different volume ratios of titanium and beryllium. These and the reference configurations are shown in Fig. 2. One should note that the measured lattice strains will be an average over the entire sampled volume. We have thus, presented the averaged results at a dimension equivalent to the midpoint, from the interface, of the sampled volume.

Preliminary analysis of the experimental data was done using a Rietveld refinement that fits all of the lattice peaks simultaneously. Anisotropic elastic constants and potential textures were not accounted for by this method. The 45° strains that we show, in Fig. 3, are volumetric and calculated from those in and normal to the basal planes of the hexagonal titanium and beryllium. Data from both the + and - 90° detectors are given. One can see that the only indication of residual strains are in the beryllium from the + 90° detector at distances of 0.25 and 0.29mm from the interface. At distances of 0.5mm or greater from the interface none of the measurements, from either detector, indicated residual strain. One should note that the minimum average distance, from the interface, that we examined in the titanium was 0.5mm. This is because the Ti is a very weak diffracting element, compared to Be, and even at 0.5mm ($\approx 360\text{mm}^3$ of diffracting material) the count times were long to obtain even a small signal.

Our data very near the interface, in the beryllium, is not consistent between the $\pm 90^\circ$ detectors. Both detectors should have, at a minimum, produced the same trends if not the same absolute numbers. The disagreement could possibly be the result of the Rietveld analysis. We will be conducting analysis of individual diffraction peaks to examine this disparity. The interface strains, and hence residual stresses, will be either small or relatively large depending on which detectors data is correct.

Figure 2 Volumes of material sampled in these experiments.

Figure 3 The experimentally measured 45° volumetric strains from both the 0° and 90° detectors.

References:

Instrument used: <i>(please type)</i> NPD	Local contact: M. Bourke	Proposal number: <i>(for LANSCE use only)</i> 5074
Title: Phase Identification of Shock -Loaded Deuterated Ice		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: A. J. Gratz High-Pressure Sciences Center, Lawrence Livermore National Laboratory, Livermore, CA 94550 K. Bennett Department of Geology & Geophysics UC Berkeley, CA 94720-4767 M. Bourke LANSCE		
Experiment report: <p>We have been using the Neutron Powder Diffractometer (NPD) to determine the phase of shock loaded D₂O ice (for phase diagram of ice, see Figure 1). The High Pressure Sciences Center at Lawrence Livermore National Laboratory (LLNL) has been devoting recent efforts to introduce laboratory study of meteor impacts on icy bodies of the outer solar system by shock loading ice specimens, and examining the possibility of achieving the amorphous state at low temperature. Water ice is an abundant material in many satellites of the outer solar system. For example, Callisto, Jupiter's moon, is 50% by weight water ice and has a highly cratered surface. The irreversible transition from ice I to its non-crystalline forms has already been studied in the laboratory at similar low temperatures and high pressures as in our experiments but by static compression as indicated by solid arrows in Figure 1. The neutron diffraction results suggest that shock loading is too dynamic a process to achieve the amorphous state.</p> <p>The samples were 2.54 cm in diameter and 0.3 cm thick discs of polycrystalline D₂O ice. We deuterated the samples to avoid high incoherent scattering of hydrogen. The ices were shock loaded in the two-stage light gas gun at LLNL. Dots in Figure 1 represent peak pressures of 6, 12, 15, 24, and 50 Kbars. Samples were mounted with the axis of the shock front perpendicular to the incident beam. Neutron diffraction at the Manuel Lujan Jr., Neutron Scattering Center at LANL enabled a collection of a complete powder pattern almost instantaneously and neutron penetration through not only the 1/4" thick aluminium capsules but the entire bulk samples.</p> <p>We were able to measure four out of the five ices. Corresponding diffraction patterns are shown in Figure 2 and the relevant crystalline ice peaks are indicated. We found no evidence for amorphization. The results were extremely surprising and not expected. Of course we have to consider that the samples melted and refroze during shock. We have calculated the Hugoniot for ice at 77K and they do not intersect the melting curve during the loading path. Theoretically, if amorphization occurred, the phase should still be present.</p> <p>We compare the microstructures of the samples to the diffraction patterns which we did not think would be possible without damaging the samples. We examine the actual ices for original grain structure. We use mechanical imprints in the aluminium capsule faces to study shock features. Each sample has vastly different microstructures (see D₂O 5, the 50 Kbar shot in Figure 3), adding a new dimension to our neutron diffraction results.</p> <p>Results of this work were presented at the Annual Fall Meeting of the American Geophysical Union and were encouraged by the community for further investigation [Bennett <i>et al.</i>, 1992].</p>		

Experiment report (continued):

Fig. 1.

Fig. 2.

a

b

Fig. 3.

Fig. 1. H_2O phase diagram [from Hemley *et al.*, 1989].

Fig. 2. Neutron diffraction patterns measured at LANSCE. Shot specimens and corresponding peak pressures are indicated at the top left corner of each pattern.

Fig. 3. Shot specimen microstructures. (a) Ice specimen surface. (b) Aluminium capsule, replicating ice specimen surface at the front of the shock wave.

References:

Bennett, K., Wenk, H.-R., Gratz, A., Nellis, W. B., Bourke, M., and Goldstone, J. A. Shock loaded low-temperature D_2O Ice, *EOS Trans. AGU*, 73, No.43,326, 1992.

Hemley, R. J., Chen, L. C., and Mao, H. K. New transformations between crystalline and amorphous ice, *Nature*, 338, 6217, 1989.

Instrument used: <i>(please type)</i> NPD	Local contact: M. Bourke, A.C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 5075
Title: Texture Measurement of Experimentally Deformed High-Pressure D ₂ O Ice		Report received: <i>(for LANSCE use only)</i> 2/23/93
Authors and affiliations: K. Bennett Department of Geology & Geophysics, UC Berkeley, CA 94720-4767 H.-R. Wenk Department of Geology & Geophysics, UC Berkeley, CA 94720-4767 W. B. Durham Experimental Geophysics Group, Lawrence Livermore National Laboratory, Livermore, CA 94550 S. H. Kirby Branch of Tectonophysics, US Geological Survey, Menlo Park, CA 94025 M. Bourke LANSCE A. C. Lawson MST-5 J. A. Goldstone LANSCE		
Experiment report: <p>We have devoted the past two years measuring texture development in high-pressure, low-temperature ice using the Neutron Powder Diffractometer (NPD) at LANSCE. The project is part of an extensive study started 12 years ago by Lawrence Livermore National Laboratory (LLNL) to characterize the rheology of ice for understanding natural deformations of ice on Earth and in the outer solar system. Other groups such as the US Geological Survey and U Minnesota have joined the study and the project is now producing most of the leading mechanical research for ice I, its polymorphs, and its clathrates [Durham <i>et al.</i>, 1992; Kirby <i>et al.</i>, 1991]. It was an honor when we were approached at UC Berkeley in 1990 by this research group as texture specialists and asked to be responsible for the measurement of the texture in ice.</p> <p>To measure the preferred orientation, we chose LANSCE as a neutron scattering facility because it has the advantage of time-of-flight neutrons. Neutron diffraction is the best method for this analysis. Neutrons provide bulk sample measurement (1.0" diameter, 1.0" long, cylindrical samples) at cryogenic temperatures. Ice has commonly been studied by neutron diffraction but never for texture measurement.</p> <p>We spent a year designing the pilot experiment in 1991 and preparing deuterated samples to avoid the incoherent scattering of hydrogen. We measured one sample and a standard sample in summer 1991. A diffraction pattern for sample 304 deformed in the intermediate flow regime from the minus 90 degree detector bank is shown in Figure 1. Three sharp peaks appear between 3 and 4 Å and could be identified. In this first pilot experiment we were not aware that we would not be able to combine the intensity data of the four detector banks. This was the reason for another year of the experiment. We redesigned the experiment to maximize measurement efficiency and to eliminate volume and absorption corrections. Unfortunately this year ice peaks intensities between 3 and 4 Å were barely visible. Figure 2 shows a diffraction pattern of sample 321 which is the same starting material as sample 304 in Figure 1 and deformed at identical pressure, temperature, and strain rate conditions. Both figures are collected from the same orientation of the sample. Despite graciously allotted beam time by LANSCE for this second year, much of the run time was spent deciphering why ice I diffraction peak intensities were so low. Other samples had similar undefined peaks of much lower intensities within the 3 to 4 Å d-spacing range, which is diffracted by the 90 degree detector banks. Ultimately, the poor quality of the spectra in 1992 were attributed to malfunctioning of the electronics. Moreover, because counting statistics were poor, we were unable to obtain polefigures of sample 327.</p>		

Experiment report (continued):

Figure 3 shows a diffraction pattern of sample 327 between 3 and 4 Å collected at LANSCE where poor counting statistics prevented polefigure collection. Two months later, the same unaltered, uncut sample was measured at National Institute of Standards (NIST) and quantitative polefigures obtained from which orientation distribution functions could be calculated. The experimental and recalculated polefigures compare very well as illustrated in Figure 4.

We are disappointed that unreliable beam and instrumentation inhibited the potential advantages of time-of-flight experiments at LANSCE for texture determination of ice.

Fig. 1.

Fig. 2.

Fig. 1. Neutron d-spacing spectra of ice I, sample 304 collected at LANSCE in summer 1991. Three sharp peaks are identified as (100), (002), and (101). Sample orientation is parallel to the incident beam.

Fig. 2. Neutron d-spacing spectra of ice I, sample 321 collected at LANSCE in summer 1992. Sample orientation is parallel to the incident beam. Three characteristic ice peaks (100), (002), and (101) can be identified but are barely visible.

Fig. 3. Neutron d-spacing spectra of ice I, sample 327, measured at LANSCE in summer 1992.

Fig. 4. Pole figures of ice I, sample 327, measured by neutron diffraction at NIST in November 1992. (a) Experimental polefigures, (100), (002), and (101) poles. (b) Recalculated polefigures, (100), (002), and (101) poles, from orientation distribution functions. Densities are represented in multiples of a random distribution (m.r.d.)

Fig. 3.

Fig. 4.

References:

- Durham, W. B., Kirby, S. H., Stern, L. A., Effects of dispersed particulates on the rheology of water ice at planetary conditions, *J. Geophys. Res.*, 97, 20,883-20,897, 1992.
- Kirby, S. H., Durham, W. B., Beeman, M. L., Heard, H. C. and Daley, M. A., Inelastic properties of ice I_h at low temperatures and high pressures, *J. Phys.*, 48, suppl., 227-232, 1987.

Instrument used: <i>(please type)</i> NPD	Local contact: Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5092
Title: To determine the structure of $\text{Pr}_{11}\text{O}_{20}$		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: L. Eyring, Dept of Chemistry & Biochemistry Arizona State University, Tempe, AZ J. Zhang, same R.B. Von Dreele LANSCE		
Experiment report: <p>During 1992 we conducted a neutron diffraction experiment on $\text{Pr}_{11}\text{O}_{20}$, continuing structural investigation of the $\text{R}_n\text{O}_{2n-2}$ homologous series of oxides ($\text{R} = \text{Ce}, \text{Pr}, \text{Rb}$). Although our previous room temperature studies on the other intermediate phases were successful, a high temperature neutron diffraction was required for $\text{Pr}_{11}\text{O}_{20}$ as it quickly decomposes to other phases during quenching.</p> <p>A ten-gram sample with the nominal composition of $\text{Pr}_{01.818}$ was sealed into a thin-walled EPR tube under 61 Torr O_2 at 25°C. The fused silica container thus prepared was placed in an evacuated furnace fitted into the high-resolution instrument (NPD). Four time-of-flight spectra with the detectors at 2θ of 90° and 148° were accumulated for 48 hours after the furnace had stabilized at 465°C.</p> <p>Attempts were made to determine the structure of $\text{Pr}_{11}\text{O}_{20}$ through Rietveld analysis facilitated by GSAS. The background coefficients and diffractometer parameters were refined by assuming a triclinic fluorite cell. Even though the data were acquired at an elevated temperature and the sample was sealed in a fused silica container, the superstructure lines were clearly visible after the background subtraction. Further testing indicated that these superstructure lines were unique, and could not be assigned either to $\text{Pr}_{12}\text{O}_{22}$, or $\text{Pr}_{10}\text{O}_{18}$, or a mixture of these two neighboring phases of $\text{Pr}_{11}\text{O}_{20}$.</p> <p>Efforts were then made to verify the space group of $\text{Pr}_{11}\text{O}_{20}$. Unfortunately, since the reflections with small d-spacings were numerous and severely overlapped, and those with larger d-spacings had very low signal/noise ratio, the space group could not be determined. Based on the observation that the cell of $\text{Pr}_{11}\text{O}_{20}$ only differs from those of its neighbors in the b axis, it was assumed that the space group for $\text{Pr}_{11}\text{O}_{20}$ was $\text{P}2_1/\text{c}$, the same as those for $\text{Pr}_{10}\text{O}_{18}$ and $\text{Pr}_{12}\text{O}_{22}$. The statistics indicated that the superstructure reflections could be better accounted for by the monoclinic cell for $\text{Pr}_{11}\text{O}_{20}$ ($a = 6.7\text{\AA}$, $b = 42.5\text{\AA}$, $c = 15.5\text{\AA}$, $\beta = 125.2^\circ$, $V = 3606\text{\AA}^3$).</p>		

Experiment report (continued):

Several models for $\text{Pr}_{11}\text{O}_{20}$ in $P2_1/c$ were developed based on the assumption that the structure of $\text{Pr}_{11}\text{O}_{20}$ might be an intergrowth of $\text{Pr}_{10}\text{O}_{18}$ and $\text{Pr}_{12}\text{O}_{22}$. With a different vacancy arrangement, each of these models contained 22 unique Pr atoms and 40 unique O atoms. In order to avoid pseudo-symmetries, atoms in the vicinity of vacancies were distorted from the ideal fluorite positions according to the patterns previously observed for the related intermediate phases. However, the refinement of the atomic positions led to unreasonable short inter-atomic distances, regardless of the differences in the initial models.

Although the structural analysis is incomplete on $\text{Pr}_{11}\text{O}_{20}$ at this point, it is believed that the problem was not due to the high temperature diffraction experiment, rather to the uncertainty of the space group, insufficient modeling, and perhaps too numerous variables. Considering the size of the unit cell, it is conceivable that the information provided by the powder diffraction experiment is inadequate for a full structure determination of $\text{Pr}_{11}\text{O}_{20}$. Yet, further progress is expected if the space group of $\text{Pr}_{11}\text{O}_{20}$ can be verified through other methods. In addition, the current attempts to unveil the structural principles underlying the ordered intermediate phases will certainly benefit the future modeling efforts on $\text{Pr}_{11}\text{O}_{20}$. Again, it is important to realize that this high-temperature neutron diffraction study will continue to play a vital role in the final determination or confirmation of the structure of $\text{Pr}_{11}\text{O}_{20}$.

References:

Instrument used: <i>(please type)</i> NPD	Local contact: Dr. R. B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5098
Title: Rietveld Structure Refinement of Diffuse Phase Transition Ferroelectrics		Report received: <i>(for LANSCE use only)</i> 4 / 1 / 93
Authors and affiliations: <p style="text-align: center;">George A. Rossetti, Jr. and Robert E. Newnham Materials Research Laboratory The Pennsylvania State University University Park, Pennsylvania 16802</p>		
Experiment report: <p>One of the most studied aspects of ferroelectric phase transitions concerns the extreme broadening of the transition anomalies that is observed in compounds or solid solutions having complex chemical compositions in which foreign ions occupy crystallographically equivalent lattice sites. The break in the translational invariance of the host lattice caused by the foreign ions leads to the observation of "diffuse" phase transition (DPT) behavior that is characterized by a pronounced smearing of such properties as the spontaneous polarization, the specific heat anomaly, the refractive index, etc., that would normally exhibit abrupt changes at a ferroelectric instability.¹</p> <p>In order to systematically investigate the structural features leading to diffuse phase transition behavior, the extensive perovskite-structured solid solution between lead titanate and lanthanum titanate was investigated. The end member lead titanate is representative of a large family of oxygen octahedra ferroelectrics that undergo normal discontinuous phase transitions from a centrosymmetric cubic prototype ($Pm\bar{3}m$) to a tetragonal ferroelectric phase ($P4mm$) of the type characterized by the condensation of a Brillouin zone-center optic lattice mode. The aliovalent substitution of lanthanum (III) for lead (II) decreases the crystal tetragonality, dramatically reduces the characteristic first-order discontinuity of the transition, and ultimately diffuses the phase transition.^{2,3}</p> <p>Prior to the experiments at LANSCE, high-temperature X-ray diffraction data were taken at the National Institute of Standards and Technology on samples of general formula</p>		

Experiment report (continued):

where the lead elimination factor $\alpha = 1.5$ and the fraction of lanthanum dopant varied in the range $y = 0.00 - 0.15$. Careful fitting of selected hkl reflections to split Pearson VII distributions revealed that systematic changes in the diffraction profile breadth and symmetry occurred as a function of both temperature and composition (y).

To eliminate the possibility that these observations were associated exclusively with particle surface effects, and to investigate the possibility of additional low-temperature lattice instabilities, powder neutron diffraction data on specimens with $y = 0.02$ and $y = 0.10$ were collected on the NPD. The data were collected at 300 K, 200 K, and 10 K using the $\pm 90^\circ$ and $\pm 148^\circ$ detector banks and the data collection time at each temperature was approximately six hours. Approximately 10 g of sample was required to completely fill the specimen canister.

Preliminary analysis of the NPD data suggests that, as observed with pure lead titanate⁴, the symmetry of the ferroelectric phase remains tetragonal at temperatures as low as 10 K. As with the X-ray data, the two samples investigated showed differences in the shapes and breadths of the diffraction profiles. Subsequent analysis of these samples by *in situ* transmission electron microscopy indicated that the profile changes are associated primarily with a nonuniform modulation of the tetragonal c -axis occurring on a nanometric length scale. Because of this additional complication, refinement of the structure by the Rietveld technique is not straightforward. However, it is hoped that the excellent resolution of the LANSCE spectrometer evident at small d -spacings will enable the static and dynamic aspects of the structure to be separated, and that a more quantitative average picture of the atomic displacements associated with these modulations can be established. Furthermore, since the neutron scattering factor for titanium is negative, it may be possible to determine whether or not any lanthanum (III) and/or lead (IV) incorporates on B-site of the perovskite structure. More detailed analysis of the combined X-ray and neutron diffraction data is currently in progress.

References:

1. M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford (1977).
2. D. Hennings and K. H. Härdtl, *Phys. Stat. Sol.* (a) **3** 465 (1970).
3. K. Keizer, G. J. Lansink, and A. J. Burggraaf, *J. Phys. Chem. Solids* **39** 59 (1978).
4. A. M. Glazer and S. A. Mabud, *Acta. Cryst.* **B34** 1065 (1978).

Instrument Used: <i>(please type)</i> NPD	Local Contact Mark Bourke	Proposal Number: <i>(for LANSCE Use Only)</i> 5122
Title: <i>In situ</i> strain measurement in an AlTiC Composite during loading		Report received: <i>(for LANSCE Use Only)</i> 4/12/93
Authors and affiliations: <p style="text-align: center;"> M.A.M. Bourke, LANSCE/MST5, MS H805 (665 1386) J.A. Goldstone, LANSCE, MS H805 (667 3629) N. Shi LANSCE/CMS, MS H805 (667 2944) M.G. Stout, MST5, MS G730 (667 6750) A.C. Lawson, MST5, MS G730 (667 8844) J.E. Allison. Ford Mo Co, (313 845 7224) </p>		
Experiment report: <p>Measurement of residual and applied strains in metal matrix composites using neutron diffraction is becoming increasingly prevalent because of the ability of this technique to identify the mean phase strain in each constituent. At a spallation source like LANSCE a specimen is scanned in wavelength to collect a complete Bragg pattern by a detector in a fixed geometry. The scattering vector for each reflection lies in the same direction in the specimen. This is important for stress measurement because it means that the direction of strain measurement for each reflection is in the same direction in the specimen. Determination of the strain for many lattice reflections offers a comprehensive assessment of the microstructural stress state and can identify crystalline anisotropy. Thus multiphase and composite problems are often handled more effectively using pulsed rather than monochromatic neutrons.</p> <p>By employing a dedicated stress rig on the NPD at LANSCE we complemented a set of residual stress measurements on aluminum titanium carbide (1) by also measuring the strain during applied loading. On the NPD a favorable diffraction geometry offers simultaneous strain measurement parallel, perpendicular, and at $\approx 60^\circ$ to the loading direction. The specimen orientation relative to the neutron beam is shown in figure 1. The loading axis is horizontal and at 45° to the incident beam allowing simultaneous axial and transverse measurements using opposing 90° detectors.</p>		
<div style="text-align: center;"> <p>Figure 1</p> </div>		

Experiment report (continued):

The material that we examined was 15vol% TiC in an artificially aged Al2219 alloy. A cylindrical specimen (10mm diameter) was loaded in uniaxial tension. Measurements were made at the following static tensile loads:

0-50-100-148-198 - 0 - 199-238-290-327 - 201-102-0 MPa.

The loading sequence was selected to keep the specimen initially in the elastic region then was followed by an increase in load sufficient to give 1% total strain at 327 MPa. On removal of the final load the specimen was exhibited a permanent strain of $\approx 0.67\%$. The hold duration at each stress level was typically 4 hours.

The strains parallel to the loading direction are shown above. Note the distinct behavior of the stiffer TiC particles and the more compliant aluminum. Anisotropic strains perpendicular to the loading direction were noted in the aluminum. Permanent peak broadening was recorded for the aluminum and there were small apparently reversible variations in the width of the TiC particles during loading.

References:

1. LANSCE Experiment report 1992 (this publication) for experiment 5033
2. "Strain measurement in individual phases of an Al/TiC composite during mechanical loading" Bourke et al., Res. Stresses in Composites: Proceedings 122nd TMS Annual Meeting, Feb. 1993
3. "Measurement of the strain in individual phases of Aluminum Titanium Carbide during loading and comparison with prediction" Bourke, Goldstone et al Scripta Metallurgica in preparation.
4. "Influence of thermal residual stresses on the development of the average lattice elastic strain during external loading in an AlTiC composite" Shi et al Met Trans in preparation

Instrument used: (please type) NPD	Local contact: Robert Von Dreele	Proposal number: (for LANSCE use only) 5153
Title: STRUCTURAL CHANGES ACCOMPANYING HEATING OF THE RHO-FRAMEWORK: HIGH TEMPERATURE STUDY OF TI-EXCHANGED BePO-RHO.		Report received: (for LANSCE use only) 4/1/93
Authors and affiliations: J. B. Parise, ESS, SUNY, Stony Brook , D. Corbin, L. Abrams, G. Jones, E.I. Du Pont, Tina M. Nenoff and Galen D. Stucky, Chemistry, UC, Santa Barbara, and R. B. Von Dreele, LANSCE.		
Experiment report: <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>The molecular sieve RHO is known to crystallize from aluminosilicate, BePO-, BeAsO and gallate compositions¹. This framework is comprised of a body centered cubic arrangement of truncated cubo-octahedra or α-cages linked <i>via</i> double 8-rings (D8R; Fig 1). A number of investigations of the aluminosilicate form of RHO have found this framework exhibits atypical flexibility²⁻⁴. Under different conditions of cation exchange, temperature and degree of hydration^{3,5,6} either the centrosymmetric or non-centrosymmetric forms of AlSiO-rho can occur. For the BeAsO- and BePO-forms, strict alternation of the cations occurs throughout the framework thereby removing the mirror plane in (110) and lowering the symmetry to $I23$. For AlSiO-rho, the centrosymmetric and non-centrosymmetric variants possess symmetry $Im\bar{3}m$ and $I\bar{4}3m$, respectively^{7,8}.</p> <p>A simple parameter, Δ, which relates the degree of ellipticity (Fig 1) of the single 8-ring (S8R) to the unit cell distortion was introduced early on in these studies⁴. Conditions leading to unit cell expansion, such as hydration, high temperatures and the exchange of large extra-framework cations, result in lower values of Δ. Unit cell contraction, due to dehydration or the replacement of (Si/Al) in the framework by smaller cations such as Be and P, results in larger values of Δ. Previous publications noted the extraordinarily large values of Δ/a sustained by the non-centrosymmetric structure of BePO-rho.</p> <p>While the majority of RHO materials possess cubic cell parameters between 14 and 15Å, those for dehydrated BePO-rho are close to 13Å. Most structural studies have been carried out on</p> </div> <div style="width: 45%; text-align: center;"> <p>Figure 1: Zeolite RHO, D8R-site for $I23$.</p> </div> </div>		

Experiment report (continued):

materials from the AlSiO-class; there is little information available to define the distortion of the framework between 13 and 14 Å⁸. In order to better define this region, ion exchange and high temperature experiments to vary the cell volume BePO-rho have been carried out.

For experiments at LANSCE, a sample of Tl-exchanged BePO-rho was studied at 110, 300, and 450°C in a vacuum furnace. Values of the distortion parameter Δ , derived from Rietveld structural refinements⁹ for data collected at 30, 110 and 300°C, are summarized in Figure 2.

Compared to data from previous studies^{7,10}, the results from this work confirm:

- 1) the straight line relationship between Δ/a and a .
- 2) the greater flexibility, as a function of temperature, of the BePO's exchanged with singly charged extra-framework cations (Fig 2).

At 450°C the powder diffraction pattern contains contributions from at least two phases, with diffraction patterns related to RHO. The possibility of a transition of the type reported¹¹ for Cd-exchanged AlSiO-rho is being investigated.

Figure 2. Variation of distortion parameter, Δ/a , a measure of the ellipticity of the pore opening shown in Fig 1, for various BePO-rhos studied; Δ decreases as the cubic unit cell parameter increases. The line is a guide to the eye.

References:

- (1) Meier et al., *Atlas of zeolite structure types*; Butterworths: London, 1986.
- (2) Baur et al., *Z. Kristallogr.* **1987**, *179*, 281-304.
- (3) McCusker et al., 6th Inter. Zeolite Confer., Butterworths: Reno, NV, 1984, pp 812-822.
- (4) Parise, J. B.; Prince, E. *Mat. Res. Bull.* **1983**, *18*, 841-852.
- (5) Parise et al., *J. Phys. Chem.* **1984**, *88*, 2303-2307.
- (6) Corbin et al., *J. Amer. Chem. Soc.* **1990**, *112*, 4821-4830.
- (7) Parise et al., *Zeolites* **1992**, *12*, 360-368.
- (8) Corbin et al., *Zeolites* **1991**, *11*, 364-367.
- (9) Larson, A. C.; Von Dreele, R. B. "GSAS manual," Los Alamos, 1986.
- (10) Parise et al., *Zeolites* **1993**, in press.
- (11) Parise et al., *J. C. S., Chem. Commun.* **1991**, *3*, 162-163.

Instrument Used: <i>(please type)</i> NPD	Local Contact Ed Ong	Proposal Number: <i>(for LANSCE Use Only)</i> 5169
Title: A Neutron and X-ray Diffraction Study of $\text{Ni}_{0.82}\text{Cu}_{0.18}\text{Cr}_2\text{O}_4$ and $\text{Ni}_{0.18}\text{Cu}_{0.82}\text{Cr}_2\text{O}_4$		Report received: <i>(for LANSCE Use Only)</i> 4/5/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> E.W. Ong D. Reinen B.L. Ramakrishna J.A. Goldstone </div> <div style="width: 65%;"> LANSCE, LANL Fachbereich Chemie der Universitat Marburg Dept. of Chemistry, Arizona State University LANSCE, LANL </div> </div>		
Experiment report: <p>Cooperative Jahn-Teller (J-T) effects play an important role in inducing the structural phase transition of many compounds containing ions with specific electronic configurations. This is particularly prevalent for those with d^4, d^9, and low-spin d^7, where their electronic states are strongly coupled to the vibrational modes of the lattice. The divalent copper ion, with a d^9 configuration, is a classic example of this. In our present study, we are investigating the effects of mixing two J-T active ions in the chromites (MCr_2O_4). Nickel and copper ions are mixed in a $\text{Ni}_x\text{Cu}_{1-x}\text{Cr}_2\text{O}_4$ solid solution where the J-T distortions of the former competes with those of the latter. Nickel was chosen because the J-T effect on Ni^{2+} is weaker than that for Cu^{2+}. The Ni^{2+} ion is also flexible in adopting various coordination geometries.</p> <p>Powder neutron diffraction experiments were proposed for two cooperative Jahn-Teller compounds this year. The compositions of these ceramic materials were $\text{Ni}_{0.82}\text{Cu}_{0.18}\text{Cr}_2\text{O}_4$ and $\text{Ni}_{0.18}\text{Cu}_{0.82}\text{Cr}_2\text{O}_4$. Due to scarcity of available neutron time, only the former compound was studied. Diffraction data were obtained using the high resolution Neutron Powder Diffractometer (NPD), housed in the Los Alamos Neutron Scattering Center (LANSCE), at Los Alamos National Laboratories. The $\text{Ni}_{0.82}\text{Cu}_{0.18}\text{Cr}_2\text{O}_4$ compound was examined at two temperatures, namely 15 K and 300 K. An experiment at 400 K was canceled because the furnace which fits into the NPD was not available during the time allotted. Powder x-ray diffraction experiments were also performed for this compound at 300 K. The diffraction data were analyzed using the Generalized Structure Analysis System (GSAS) software package, developed at LANSCE. This program can determine the crystalline and magnetic structure of the compound using neutron and x-ray data sets.</p> <p>The crystal structure of the compound was found to be tetragonal, represented by the space group $I4_2d$, at ambient temperature. A summary of structural parameters is listed below:</p> <p style="margin-left: 40px;">space group: $I4_2d$</p> <p style="margin-left: 40px;">lattice parameters: $a = b = 5.928(14) \text{ \AA}$ $c = 8.167(19) \text{ \AA}$</p>		

Experiment report (continued):

atom type	x	y	z	occupancy	Wykoff Pos.
Ni	0	0	0	0.82	4a
Cu	0	0	0	0.18	4a
Cr	0.5096	1/4	1/8	1.00	8d
O	0.2756	0.0026	0.1318	1.00	16e

This result was surprising. The compound's high nickel content would have led one to expect its crystal structure to be closer to NiCr_2O_4 , with a space group of $I4_1amd$. Instead, its structure is similar to CuCr_2O_4 , which is described by $I42d$. Refinement of the compound's structure is still in progress at this time. Strong anisotropy was observed in the diffraction pattern. Bragg peaks corresponding to reflections from the 202 and 404 planes were much narrower than others. Anisotropic strain broadening and anisotropic thermal displacement of the atoms will be invoked in further structural refinement using the data.

The compound was found to under a tetragonal-to-orthorhombic phase transition on cooling. Several of the peaks in the tetragonal diffraction pattern were found to split into multiple peaks in the low temperature data. Analysis of this data is underway. Low temperature x-ray data is needed to determine if any of the peaks observed in the neutron diffraction pattern arise from magnetic scattering, due to long-ranged antiferromagnetic ordering of the magnetic moments within this compound. In the absence of magnetic peaks, we can more confidently attribute the splitting to the orthorhombic phase transition.

We will attempt to perform the 400 K experiment, mentioned above, during the 1993 LANSCE run cycle. We anticipate observing the cubic phase at this temperature.

References:

Instrument used: (please type) NPD	Local contact: Joyce A. Goldstone	Proposal number: (for LANSCE use only) 5400
Title: Thermal Expansion of η -Pu _{0.90} Np _{0.10}		Report received: (for LANSCE use only) 2/22/93
Authors and affiliations: Joyce A. Goldstone, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 A. C. Lawson, MST-5, Los Alamos National Laboratory, Los Alamos, NM 87545 Barbara Cort, NMT-5, Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>In 1989, we attempted to determine the crystal structure of η-Pu_{0.90}Np_{0.10} using neutron powder diffraction on GPPD at IPNS. This phase is only stable at high temperatures, between approximately 325° and 450° C. Then we obtained data during an experiment at 375° C. The diffraction pattern was extremely complex in agreement with available x-ray data. We were unable to solve the crystal structure from these data. We proposed to study this sample at three more temperatures: 350°, 400°, and 450° C. We hoped to learn two things from these new data. First, we can verify that the alloy is really single phase at high temperatures, in agreement with the published phase diagram. Second, we can determine the thermal expansion coefficient for each peak in the diffraction pattern. We expect the highly anisotropic thermal expansion behavior that is characteristic of the light actinide elements to be reflected in these data.</p> <p>Data were collected on the Neutron Powder Diffractometer (NPD) at LANSCE during the 1992 run cycles. Four temperatures were studied, in the following sequence 350°C, 450°C, 400°C in the η-phase region and finally 290°C in the β-phase region of the phase diagram[1]. Figures 1-4 on the following page show the diffraction patterns obtained for the η-phase on the NPD and GPPD. Diffraction patterns at the three lowest temperatures are nearly identical, indicating that it is unlikely that the sample is multiphase. However, at 450°C, some peaks appear to split, indicating a structural change. Figures 5 and 6 show a selected region of the diffraction patterns from 400°C and 450°C. It is evident that the peak at 2.576 Å has separated into two peaks with an approximately ratio of 1:2 in intensities. Similar behavior is seen in a peak at 1.531 Å. In addition, a new peak is observed at 2.552 Å. These peaks are not from the epsilon structure, which occurs at slightly higher temperatures according to the published phase diagram. All these tantalizing hints have not yet enabled us to solve the crystal structure of this alloy, but work is continuing.</p>		

Experiment report (continued):

Figure 1: PuNp data at 350° C

Figure 2: PuNp data at 375° C

Figure 3: PuNp data at 400° C

Figure 4: PuNp data at 450° C

Figure 5: PuNp data at 400° C

Figure 6: PuNp data at 450° C

References:

- [1] P. G. Mardon, J. H. Pearce, and J. A. C. Marples, "Constitution Studies on the Npetunium-Plutonium Alloy System," *J. Less-Common Metals*, 3 (1961) 281-292.

Instrument Used: (please type) NPD	Local Contact Mark Bourke	Proposal Number: <i>(for LANSCE Use Only)</i> 5701
Title: Residual strain measurement in a Ti 24 11 SCS6 08 MMC		Report received: <i>(for LANSCE Use Only)</i> 4/12/93
Authors and affiliations: <p>M.A.M. Bourke, LANSCE/MST5, MS H805 (665 1386) M.R. James, Rockwell International Science Center (805 373 4230) J.A. Goldstone, LANSCE, MS H805 (667 3629) A.C. Lawson, MST5, MS G730 (667 8844)</p>		
Experiment report: <p>This experiment was performed to complete a study, commenced in 1991, of residual stresses in Ti continuous fiber SiC systems.</p> <p>Metal matrix composites (MMCs) develop residual strains after consolidation due to the thermal expansion mismatch of the reinforcement fibers and the matrix. The stresses are often examined using X ray diffraction but one recurrent problem is verifying that the surface measurements accurately portray the state of stress in the fiber/matrix region of the interior (1,2). Neutrons penetrate more effectively than X rays in most materials of engineering interest and provide bulk residual strain measurements in continuous fiber composites. Consequently comparison of the two techniques can validate the X ray measurements.</p> <p>Measurements have been made on four systems:</p> <ul style="list-style-type: none"> • SiC / Ti-6Al-4V [O]₈ • SiC / Ti-24Al-11Nb [O]₈ (two different matrix foils) • SiC / Ti-25Al-10Nb-3V-1Mo [O]₃ <p>Equivalent monolithic samples of the metal alloys and a mat of the SiC fibers were also examined. The thickness of the TiSiC sheets varied between 1 and 3 mm and the total sampling volume between 500 and 2000mm³. Count times were typically 8 hours per run. Although the SiC fibers in the reference mat for the standard constituted a small volume (<10mm³)- because of the texture in the fibers there were nevertheless strong diffracted reflections from which strains could be measured. The figure shows the compressive and tensile strains in the SiC and Ti respectively for the Ti-24-11 system examined in 1992.</p>		

Experiment report (continued):

Our results from 1991 and 1992 indicate that for thick (>6 ply) composites X ray surface stress measurements of the residual stress in the titanium do adequately describe the state of longitudinal stress. This is not true for thin (3 ply) systems in which the stress has been shown to be not uniform through the thickness. This non uniformity may be a result of non symmetric lay-up or to the thin nature of the composite. However most continuous fiber MMCs have symmetric lay-ups which equal or exceed six plies. The magnitude of the compressive stress measured in the SiC fibers compares well with values measured by independent means.

References:

1. M.R. James, International conference on residual stress 2, Pbl'd Elsevier, pp429-35 (1989).
2. B.N. Cox et al, Met Trans. A 21A:2701-2707 (1990)
3. M.R. James et al, Adv in X-ray analysis Vol 36 (in press)
4. M.R. James et al, Residual Stress in Composites, Proceedings of 122nd TMS annual meeting (in press).

LANSCE file photo

Single Crystal Diffractometer (SCD)

Single Crystal Diffractometer (SCD)

The Single Crystal Diffractometer (SCD) can be used to determine the crystal structures of a wide variety of materials. Neutrons are scattered from the crystalline sample into an area detector ($25 \times 25 \text{ cm}^2$; position-sensitive; ^3He gas-filled proportional counter), and the wavelength of the neutrons is determined by their time of flight from the source to the detector. To collect all the required data for a particular crystal, the orientation of the sample can be changed by rotations of the goniometer about ϕ and ω . The SCD has been used to study the structure of organometallic molecules

that show a unique binding of H_2 ; crystal-structure changes at solid-solid phase transitions; magnetic spin structure twinned or multiple crystals; the texture analysis of polycrystalline materials that have been subjected to extreme geological environments; and crystal structures of materials under pressures of 10 to 20 thousand atmospheres. The instrument measures a large volume of reciprocal space at one time and, therefore, can be used for studies of unknown incommensurate structures, diffuse scattering, etc. Nonambient sample environments can also be accommodated.

Instrument Details

Wavelength range, λ	0.5 - 10 Å
Beam diameter at sample	1 - 5 mm
Time resolution	~1%
Maximum lattice constant	~20 Å
Detector	1 multiwire proportional counter (25 cm x 25 cm) at 90°
Detector resolution	2.5 mm
Moderator	Chilled water at 10° C
Sample environment	10 K to 300° C
Sample size	0.5 - 10 mm ³
Experiment duration	2 - 4 days per octant of reciprocal space

Allen C. Larson, instrument scientist
Dennis Martinez, instrument technician

SCD Experiment reports

5019	<i>Hydrogen Bonding in the Antivirus Active Heteropolytungstate (NH₄)₁₇Na(NaW₂₁Sb₉O₈₆) • 14H₂O</i>	90
5020	<i>A Single Crystal Study of Cubic Stabilised Zirconia</i>	92
5040	<i>Crystal Chemistry of Hydrogen in Rutile of Mantle Origin</i>	94
5047	<i>The Crystallographic Fabric of Mantle Rocks Experimentally Deformed at Hypersolidus Temperatures</i>	96
5048	<i>Preferred Orientation of Quartz and Biotite in Deformed Granite</i>	98
5090	<i>Alignment Study of Superconducting BSCCO Wire (Bi₂Sr₂CaCu₂O_x and Bi₂Sr₂Ca₂Cu₃O_y)</i>	100
5091	<i>The Crystal Structure of Squaric Acid Around the Order-Disorder Transition at 512K</i>	102
5702	<i>Neutron Scattering from Neutron Irradiated Rare-Earth-doped YAG</i>	104

Instrument used: (please type) SCD	Local contact: A. C. Larson	Proposal number: (for LANSCE use only) 5019
Title: Hydrogen Bonding in the Antivirus Active Heteropoly- tungstate $(\text{NH}_4)_{17}\text{Na}(\text{NaW}_{21}\text{Sb}_9\text{O}_{86}) \cdot 14\text{H}_2\text{O}$ Prop.no. 5019		Report received: (for LANSCE use only) 3/19/93
Authors and affiliations: Christian Robl Institut für Anorganische Chemie der Universität München, Meiserstr.1, D-8000 München 2, Fed. Rep. of Germany		
Experiment report: The inorganic cryptate $(\text{NH}_4)_{17}\text{Na}(\text{NaW}_{21}\text{Sb}_9\text{O}_{86}) \cdot 14\text{H}_2\text{O}$ has been reported to possess considerable anti-viral activity (1). It has to be assumed that hydrogen bonding plays an important part in the interaction between this heteropoly compound and the biological substrate. Thus we attempted to study the proton acceptor properties of the $(\text{NaW}_{21}\text{Sb}_9\text{O}_{86})^{18-}$ anion by single crystal neutron diffraction. Furthermore it was indicated to verify the molecular structure and composition of this peculiar heteropoly anion which hitherto merely have been derived from X-ray structure analysis (2). A single crystal sealed in a glass capillary was mounted on the SCD diffractometer and cooled to as low a temperature as achievable in order to minimize thermal motion. However, due to limited beam stability and further experimental problems the quality of the recorded histograms was rather poor. Consequently these diffraction data could not furnish the desired information on the hydrogen bonding system. Nevertheless the molecular structure of the $(\text{NaW}_{21}\text{Sb}_9\text{O}_{86})^{18-}$ anion has been confirmed by this experiment (Fig.1).		

Experiment report (continued):

Fig. 1 The $(\text{NaW}_{21}\text{Sb}_9\text{O}_{86})^{18-}$ anion. The view direction is slightly inclined to the $\bar{b}$ axis of the anion. (Dotted circles=tungsten, hatched circles=antimony, shaded circles=oxygen.)

References:

- (1) W.Rozenbaum, D.Dormont, B.Spire, E.Vilmer, M.Gentilini, C.Griscelli, L.Montagnier, F.Barre-Sinoussi, and J.C.Chernan, *Lancet* (1985) 450.
- (2) J.Fischer, L.Ricard, and R.Weiss, *J.Am.Chem.Soc.* 98(1976) 3050.

Instrument used: <i>(please type)</i> SCD	Local contact: Dr Allen Larson	Proposal number: <i>(for LANSCE use only)</i> 5020
Title: A single crystal study of cubic stabilised zirconia		Report received: <i>(for LANSCE use only)</i> 12/18/92
Authors and affiliations: D.N. ARGYRIOU & M.M. ELCOMBE Australian Nuclear Science & Technology Organisation New Illawarra Road PMB 1 MENAI NSW 2234 Australia		
Experiment report: <p>To investigate the average structure of cubic stabilised zirconia (CSZ) as a function of oxygen vacancy levels, we collected single crystal time-of-flight diffraction data for a series of CSZ crystals with oxygen vacancy levels between ~ 4-10% (see table 1). To analyse and refine the data we have used the suite of programs under GSAS.</p> <p>The diffraction data was first refined assuming a perfect fluorite structure for all crystals. In these refinements the temperature factors for both the cation and anion are large, suggesting that the observed temperature parameters include a large static displacement component. We found that the observed temperature parameters and therefore the static disorder increases with oxygen vacancies (see figure 1).</p> <p>Further analysis concentrated on refining the data on the basis of models which have already appeared in the literature ¹⁻⁴, thus displacing the O-atom in the <111> or <100> directions. This led to slightly lower R factors, however the thermal parameters for the oxygen and the cations were still large, indicating that these models were not entirely successful. We used difference fourier as an aid to formulating better models for the defect structure of CSZs. The difference nuclear density map, for crystal A, centred on the oxygen (1/4,1/4,1/4) site (see figure 2) shows that the O-atoms are smeared in the <100> direction. We believe that this is not a thermal or dynamic effect, but it indicates that static displacements are not of a set magnitude but follow a distribution in the <100> direction. This is in agreement with recent diffuse scattering results ⁵. For crystals B and C difference fourier maps show similar features in the <111> directions, as well as in the <100>.</p> <p>We have attempted to model this distribution, by displacing the O-atom in the <100> or <111> and refining with anisotropic thermal parameters the static displacements. This approach was very successful in describing the low oxygen vacancy crystal A (see table 2). Currently we are working on improving our models for the high oxygen vacancy CSZs.</p>		

Experiment report (continued):

Table1: Sample Details

Crystal	Composition	% O Vacancies	α (Å) †
A	Zr _{0.826} Y _{0.174} O _{1.913}	4.35	5.158(1)
B	Zr _{0.74} Y _{0.26} O _{1.870}	6.50	5.171(3)
C	Zr _{0.61} Y _{0.39} O _{1.805}	9.75	5.186(1)
D	Zr _{0.875} Ca _{0.125} O _{1.875}	6.25	5.186(1)

† Number in paranthesis indicates the error on the last digit.

Table2: R_wF^2 for crystals A and C.

Model	Crystal	
	A	B
Fluorite	10.3	11.5
<111>	9.6	9.6
<111> _{anisotropic}	9.4	9.6
<100>	10.3	10.8
<100> _{anisotropic}	7.3	9.6

Figure 1

Figure 2

References:

1. R. E. Carter and W. L. Roth, (1968). EMF Measurement in High Temperature Systems, C. B. Alcock. New York, The Institute of Mining and Metallurgy.
2. H. Horiuchi, A. J. Schultz, P. C. W. Leung and J. M. Williams, (1984). *Acta Cryst.*, **B40**, 367-372.
3. C. J. Howard, R. J. Hill and B. E. Richert, (1988). *Acta Cryst.*, **B44**, 116-120.
4. M. Morinaga, J. B. Cohen and J. F. Jr, (1979). *Acta Cryst.*, **A35**, 789-795.
5. D. Steele and B. E. F. Fender, (1974). *J. Phys. C.*, **7**, 1-11.
6. D.N. Argiriou, M.M. Elcombe, T.R. Welberry. (to be published).

Instrument used: <i>(please type)</i> SCD (single crystal diffractometer)	Local contact: Allen C. Larson	Proposal number: <i>(for LANSCE use only)</i> 5040
Title: Crystal Chemistry of Hydrogen in Rutile of Mantle Origin		Report received: <i>(for LANSCE use only)</i> 2/1/93
Authors and affiliations: <u>R. Jeffrey Swope</u> , J.R. Smyth, (Department of Geological Sciences, University of Colorado, Boulder, CO 80309-0250) and A. C. Larson, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>Rutile, TiO_2, is a common accessory phase in eclogite and peridotite nodules in kimberlites. It is isostructural with stishovite, SiO_2, and may serve as a structural analogue for high pressure silica. Infra-red studies have shown that natural rutiles may contain up to 50,000 atoms of H per 10^6 Ti atoms. The crystal structure of a natural, hydrous rutile containing approximately 0.72 wt% Fe_2O_3, 0.68% Al_2O_3, 1.16% Cr_2O_3 and 1.86% Nb_2O_5, has been refined from neutron single crystal data collected at 24K at Los Alamos Neutron Scattering Center. Previously reported IR studies indicated that the sample contained an estimated 40,000 ppm atomic H.</p> <p>The position of hydrogen was located by examining the negative residuals in the difference Fourier. The refined position of H lies just off of the shared oxygen-oxygen edge of the octahedron at $x/a = 0.4177$, $y/b = 0.5033$, $z/c = 0$. The refined occupancy of this position is 2.8%, consistent with the H concentration estimated from IR. The OH vector lies on the mirror perpendicular to the c-axis, consistent with the IR observations. The IR absorption due to OH stretching occurs as a sharp band at approximately 3300 cm^{-1} which is strongly polarized in the omega direction (perpendicular to c).</p> <p>The crystal chemical effect of the H is both to balance the charge deficiency due to substitution of trivalent cations and to mitigate electrostatic repulsion created by the very short O-O distance along the shared edge. Stishovite has an even shorter O-O shared edge, so that it likely that a similar coupled substitution of H with Al may occur in stishovite.</p>		

Experiment report *(continued)*:

Single crystal X-ray data for a rutile taken from the same sample as the crystal used for the neutron study was compared with data for a synthetic rutile containing little or no hydrogen. Both data sets were collected on a Siemens single crystal diffractometer equipped with a rotating anode and an 18 kW generator. The refinements of these two rutiles show that there is no significant difference in the atomic positions of the nominally hydrous rutile and the dry synthetic rutile.

References:

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
SCD	A. C. Larson	5047
Title: The Crystallographic Fabric of Mantle Rocks Experimentally Deformed at Hypersolidus Temperatures		Report received: (for LANSCE use only)
		2/23/93

Authors and affiliations:

G. Y. Bussod Bayerisches Geoinstitut
Bayreuth, Germany
H.-R. Wenk Department of Geology & Geophysics
UC Berkeley, 94720-4767
A. C. Larson LANSCE
K. Bennett Department of Geology & Geophysics
UC Berkeley, 94720-4767

Experiment report:

For the past four years, the intent of this project has been to determine the preferred crystallographic orientation of polycrystalline olivine. Olivine is one of the main constituents of the upper mantle and its material properties are studied by geologists and geophysicists to help interpret upper mantle convection. Recently much study has been devoted to quantifying the rheological behavior of partial melts of olivine to study processes such as metasomatism, magma mobilization, and transport which each influence interpretation of convection in the Earth. We present neutron scattering pole figures of four polycrystalline olivine-rich rocks experimentally deformed and resulting in varying volume fractions of silicate melt. The purpose of quantitative texture analysis for these samples was to investigate the affect of melt on the structural properties of olivine. There are numerous natural polefigures already measured [Mercier, 1985]. It was proposed that perhaps solid grain interaction may be more responsible for the distribution of stress within the polycrystal when there is more melt in the the sample.

For the past four years we have worked with LANSCE to measure the texture of these samples accurately. One sample was measured in summer 1990 and three sample were measured this run cycle in summer 1992. The plan was for Gilles Bussod to supply experimentally deformed, homogenous fine-grained peridotite samples which contained partial melt. UC Berkeley was to determine the texture of the samples using the Single Crystal Diffractometer (SCD) at LANSCE.

A table of the data and description of the samples is listed below. Specific grain morphology and melt topology and distribution is described in detail by Bussod and Christie, 1991.

Experimentally Deformed Lherzolites Measured by Neutron Diffraction

Sample	vol % melt	Temperature	Confining	Strain Rate	Stress	Strain	Grain characteristics
Number	silicate	(°C)	Pressure (GPa)	(1/sec)	MPa	(%)	
GB1183	10%	1004	0.9	2.2x10 ⁻⁶	182	31	random, hot-pressed
GB1168	6%	998	1	2.1x10 ⁻⁶	246	40	highly recrystallized
GB1181	6%	985	1	1.7 x 10 ⁻⁷	199	20.5	6% glass, olivine neoblasts
GB1182	2%	890	1	1.9x10 ⁻⁷	250	15.4	2% glass, olivine neoblasts

Experiment report (continued):

The reason for measurement this second year was because large intensities were attributed to coarse grain size and because artifacts related to detector settings were not resolved. Unfortunately, samples still appear coarse grained. Also, surprisingly, we observed very uncharacteristic, symmetric pole figures not only for multiple peaks of olivine but for multiple samples (see Figure 1a-c). Moreover, this pattern matched our data collection map of the histograms (Figure 1d). In the end these new measurements were useful and we observed that a few particular low angle peaks that did not have this histogram artifact and their textures could be determined. We regret that so much time was spent to distinguish between coarse grained sample artifacts, statistical artifacts, and deconvolution artifacts and has caused such a delay in our results. We have results for the hot-pressed sample which is fine-grained (Figure 2).

Fig. 1. Measured pole figures of the experimentally deformed peridotites using the SCD at LANSCE. (a) Sample GB1183, (002) pole. (b) Sample GB1168, (210) pole, (c) Sample GB1168, (101) pole. (d) Histogram table for data collection.

Fig. 2. Measured pole figures of experimentally deformed GB1183, hot-pressed synthetic peridotite. (301), (121), and (313) poles are shown. Contours are in multiples of random distributions (m.r.d.) and dots represent densities less than 1 m.r.d..

References:

- Mercier, J.-C. C., Olivine and pyroxenes, in Preferred Orientation in Deformed Metals and Rocks: an Introduction to Modern Texture Analysis, ed. H.-R. Wenk (Academic Press, San Diego), 407-430, 1985.
- Bussod, G. Y. and J. M. Christie, Textural development and melt topology in spinel lherzolite experimentally deformed at hypersolidus conditions, *J. Petrol.*, 17-39, 1991.

Instrument used: <i>(please type)</i> SCD	Local contact: A.C. Larson	Proposal number: <i>(for LANSCE use only)</i> 5048
Title: Preferred Orientation of Quartz and Biotite in Deformed Granite		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: H.-R. Wenk, Department of Geology and Geophysics, University of California Berkeley, CA 94720 F. Heidelbach, Department of Geology and Geophysics, University of California Berkeley, CA 94720 A. C. Larson, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545		

Experiment report:

The deformation history of a rock is reflected in the preferred lattice orientation of its main components. In the deformed granites from the Santa Rosa mylonite zone quartz and biotite are the main constituents displaying typical microstructures of ductile deformation and recrystallization. In continuation of our experiments from last year (which were incomplete because of limited beamtime) we measured the textures of two highly deformed samples from the Santa Rosa mylonite zone. The main objective was to determine the preferred orientations of quartz (trigonal) and biotite (monoclinic) which form the dominant components in these rocks beside plagioclase and alkali feldspar (both triclinic).

The low sample symmetry (triclinic) requires the measurement of a complete half sphere of reciprocal space which corresponds to 27 detector positions on the SCD instrument. The wavelength distribution in the primary beam was relatively deficient of neutrons at large wavelengths so that the counting statistics for reflections at high d-spacings ($>4.5\text{\AA}$) were very poor and no meaningful pole figures could be gained in this range which would have been extremely important for these samples, e.g. to obtain pole figures for biotite (see fig. 1).

In sample PC282 the strongest quartz peaks could be identified (fig. 1) and pole figures were extracted from the histograms. The sample PC283 could not be fully measured (two histograms missing). In addition the number of neutron counts per histogram had to be reduced during the measurement because of the limited beamtime. This decreased the counting statistics and caused a poor peak to background ratio in the resulting histograms. The pole figures for quartz therefore show some irregular strong single peaks in this sample. The diffraction peaks from biotite in both samples could not be identified as clearly as those in the previous measurements. This is partly due to poor statistics at high d-spacings where some of the significant biotite peaks are located.

The quartz pole figures from both samples were used as input for the calculation of a complete orientation distribution function with the WIMV algorithm. The comparison of measured and recalculated pole figures (fig.2) proves the compatibility of the measurements for each lattice plane. In addition the distribution of poles which could not be measured (extinction) or which are overlapped with peaks from different phases can be derived from the ODF. As an example the recalculated (001) and (101) pole figure of quartz are shown in Fig.3. For both samples the quartz texture shows a c-axis maximum $\pm$ in the plane of foliation and a distribution of a-axes in a girdle perpendicular to the foliation. This texture is typical of dynamically recrystallized quartzites. The peak intensity is low (2.2x random) and the minimum intensity fairly high (0.5x random), i.e., the preferred orientation is relatively weak. This may also be caused by low counting statistics. Overall results are similar as those obtained from a related sample PC82 measured at ILL Grenoble (Wenk & Pannetier 1990).

The results presented here demonstrate that SCD provides an efficient tool for the texture analysis in polyphase rocks. Still, the reliability of the beam, the limited access time and the insensitivity at high d-spacings pose a serious problem for a complete and successful data collection of geological samples.

Fig. 1: Diffraction pattern of sample PC282 in histogram 1 (center of the pole figure). Notice the high background noise beyond 4.5Å. Strongest quartz peaks are indexed.

Fig. 2: Measured (top row) and recalculated (bottom row) pole figures for quartz in sample PC282. Projection is onto the foliation plane. Contour levels are 0.25 mrd for measured and 0.1 mrd for recalculated pole figures; areas with intensities below 1.0 are dotted.

Fig. 3 Recalculated pole figures (001) and (101) for sample PC282. Projection is onto the foliation plane. Contour levels are the same as for recalculated pole figures in Fig. 2.

Reference:

Wenk, H.-R. & Pannetier, J. (1990): Texture development in deformed granodiorites from the Santa Rosa mylonite zone, southern California. *Journal of Structural Geology*, 12: 177-184.

Instrument used: (please type) SCD	Local contact: Allen C. Larson	Proposal number: (for LANSCE use only) 5090
Title: Alignment Study of Superconducting BSCCO Wire ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$)		Report received: (for LANSCE use only) 3/10/93
Authors and affiliations: <p>Eric E. Hellstrom, Dept of Materials Science and Engineering and Applied Superconductivity Center, University of Wisconsin-Madison, Madison, WI</p> <p>Allen C. Larson, LANSCE, Los Alamos National Laboratory, Los Alamos, NM</p>		
Experiment report: <p>The SCD was used to collect data for pole figure analysis of 2212 BSCCO (Bi:Sr:Ca:Cu) high-temperature superconducting tape. The samples were prepared from Ag-sheathed BSCCO tape that had been melt processed. Melt processing leads to high alignment of the c-axis perpendicular to the plane of the tape. This alignment is thought to be critical to develop high critical current density J_c in the tapes. The neutron diffraction samples were built by stacking then gluing 30 layers of 100 μm thick by 3mm long tape to form blocks. Data were collected on two samples. Sample A was made using tape with the Ag sheath on the superconducting core, and sample B was built from tape from which the Ag sheath had been removed by electropolishing. The tapes used for samples a and b were made at different times, but were processed under nominally identical conditions.</p> <p>Sample A, which had the Ag-sheath in place, was the same sample that had been measured previously.¹ In the present study a complete hemisphere of diffraction data was collected for sample A, and the signal to noise ratio was improved by increasing the collection time for each histogram. The new pole figure for $3.83 \pm 0.05 \text{ \AA}$ (Fig. 1a) shows the multiples of random distribution (MRD) > 1 in the center of the figure. In the earlier study this had been identified as the (008) pole. However, in Fig. 1a, MRD > 1 is also present at the equator, which had not been observed in the earlier study.¹ We interpret intensity at the equator to be due to diffraction from a plane other than (008), whose d spacing is close to that of (008) ($3.86 \text{ \AA}$), and whose plane normal would be close to perpendicular to the c axis. Such a plane is (110) ($3.80 \text{ \AA}$). In our analysis of the diffraction data these peaks "overlap". Figure 1b shows the pole figure for $1.92 \pm 0.05 \text{ \AA}$. Again this shows intensity at the center and equator, which had been observed in the earlier study. However, in the earlier study this had been interpreted as being due to the (220) peak leading to the equatorial MRD > 1, and secondary alignment of the c-axis parallel to the plane of the tape for the central MRD > 1. This previous interpretation is not consistent with microstructural studies we have done since this earlier diffraction study. We now attribute the central intensity to (0016).</p> <p>A complete set of histograms was collected for sample B. Only 10 of the 27 histograms were collected during the time allotted for these experiments in Aug. 92 and the others were collected afterwards. In this sample, two 30 layer thick samples were glued side-by-side and placed in the beam. As expected, removing the Ag and significantly increasing the diffracting volume in the beam increased the diffracted signal. So far, only data collected in Aug. 92 have been analyzed. Figure 2a and 2b show the $3.83 \pm 0.05 \text{ \AA}$ and $1.92 \pm 0.05 \text{ \AA}$ pole figures, respectively. The MRDs are higher for the (008) and (0016) poles than in sample A (Figs. 1a and 1b), indicating a greater degree of alignment in this sample. The remainder of the histogram will be analyzed in the coming months. The I vs d plots show more structure in sample B than in A, so it may be possible to separate the "overlapping" poles for sample B.</p>		

Experiment report (continued):

The successful pole figure studies for sample B have significant implications for neutron diffraction pole-figure studies of Ag-sheathed 2223 tapes. Specifically, c-axis alignment in 2223 is also crucial for attaining high J_c . However, the alignment in 2223 is much lower than in melt-processed 2212, and in 2223 the alignment develops in stages during the multistep mechanical deformation/thermal heat treatment scheme needed to form 2223. The significance of the results of sample B are that we have shown how to maximize the sample volume and eliminate unwanted scattering from the Ag sheath. This should allow the alignment mechanism to be studied using neutron diffraction in 2223 tapes.

Fig. 1 Pole-figures for sample A for the (a) $3.83 \pm 0.05 \text{ \AA}$ and (b) $1.92 \pm 0.05 \text{ \AA}$ poles. Dotted regions indicate $\text{MRD} < 1$.

Fig. 2 Pole-figures for sample B for the (a) $3.83 \pm 0.05 \text{ \AA}$ and (b) $1.92 \pm 0.05 \text{ \AA}$ poles (histograms 1-6). Dotted regions indicate $\text{MRD} < 1$.

References:

- ¹ E.E. Hellstrom and P. Vergamini, report for LANSCE 1990 run cycle

Instrument used: <i>(please type)</i> SCD	Local contact: A.C.Larson	Proposal number: <i>(for LANSCE use only)</i> 5091										
Title: The Crystal Structure of Squaric Acid Around the Order-Disorder Transition at 512 K.		Report received: <i>(for LANSCE use only)</i> 4/16/93										
Authors and affiliations: <table border="0" style="width: 100%;"> <tr> <td style="width: 50%;">R.J.Nelmes</td> <td style="width: 50%;">Department of Physics</td> </tr> <tr> <td>J.S.Loveday</td> <td>The University of Edinburgh</td> </tr> <tr> <td>R.M.Wilson</td> <td>Edinburgh</td> </tr> <tr> <td colspan="2"> </td> </tr> <tr> <td>A.C.Larson</td> <td>LANSCE</td> </tr> </table>			R.J.Nelmes	Department of Physics	J.S.Loveday	The University of Edinburgh	R.M.Wilson	Edinburgh			A.C.Larson	LANSCE
R.J.Nelmes	Department of Physics											
J.S.Loveday	The University of Edinburgh											
R.M.Wilson	Edinburgh											
A.C.Larson	LANSCE											
Experiment report: <p>Two advantages of the time-of-flight Laue technique are the parallel collection of reflections within a histogram and the high flux of short-wavelength neutrons that are a characteristic of a spallation source. In this experiment we intended to make use of these features to study the structure of deuterated squaric acid ($D_2C_4O_4$ or D_2SQ) just above its hydrogen-ordering transition at $T_c=512$ K, as part of a major programme of work on the relationship between T_c and H-bond dimensions in H-ordering systems. However, on arrival at LANSCE we were informed that the cryo-furnace on SCD was not able to achieve this temperature and so it was decided to study the low-temperature structure instead. The intention was to look for evidence of residual disorder in the heavy-atom structure, by following both positional and thermal parameters as a function of temperature.</p> <p>A full quadrant of data was first collected at room temperature for comparison with data collected from the same sample at I.L.L. on the D9 diffractometer. Refinements of this t-o-f data-set gave structural parameters that were not significantly different from the previous work but the quality of fit was significantly poorer, apparently due to difficulties in modelling the extinction. This showed very strong variation over the wavelength range accessed.</p> <p>We then cooled to ~ 10 K to gauge the range of variation to be followed. To our surprise, this revealed a wholly unsuspected new phase — indicated by the presence of the 050 reflection (see Figure 1) which is forbidden by the space group adopted at room temperature ($P2_1/m$). There was also weak evidence for the 070 and possibly 030 reflections. Studies of the temperature dependence of the intensity of the 050 reflection (see Figure 2) show that the transition occurs between 90 and 125 K.</p> <p>Work is in progress to identify the true structure of the low-temperature phase. We also expect to obtain very useful results on the λ-dependence of extinction from the data sets obtained in this experiment — a matter of general importance for t-o-f single crystal work. The outcome of the unplanned direction of the experiment has thus been both interesting and valuable.</p>												

Experiment report (continued):

Figure 1: A plot of intensity versus d-spacing along $\langle 0k0 \rangle$ at 10K. The 050 reflection is marked with an asterisk (*).

Figure 2: The temperature dependence of the intensity of the 0 5 0 reflection of deuterated squaric acid.

References:

Instrument used: <i>(please type)</i> SCD	Local contact: Mike Fitzsimmons	Proposal number: <i>(for LANSCE use only)</i> 5702
Title: Neutron Scattering from Neutron Irradiated Rare-Earth-doped YAG		Report received: <i>(for LANSCE use only)</i> 12/18/92
<p>Authors and affiliations:</p> <p>Kurt E. Sickafus, Michael Fitzsimmons, Elizabeth A. Cooper, and Allen C. Larson Los Alamos National Laboratory</p>		
<p>Experiment report:</p> <p>Rare-earth doped YAG single crystals were irradiated with thermal neutrons at Omega West. Since the rare-earth dopant (Ho, Er, and Sm) has a large thermal neutron capture cross-section, it was expected that this species would be preferentially effected by the irradiation and might be displaced from its lattice position as well as transmuted. We therefore expected to see some diffuse scattering from the effected lattice positions from the single crystal neutron scattering experiment performed at LANSCE using the SCD. However, for the irradiation doses examined, no clear evidence for this was seen. This could be due to the relaxation of the rare-earth species back to its original lattice position, or due to insensitivity of the instrument to the small changes incurred.</p>

*Low-Q Diffractometer
(LQD)*

Low-Q Diffractometer (LQD)

The Low-Q Diffractometer (LQD) is designed for studying structures with dimensions in the range from 10 to 1000 Å. Examples of problems that may be addressed include the following: structures of biological membranes; DNA/protein assemblies; large virus particles; nucleation and growth of voids in radiation-damaged bulk samples; phase separation in alloys; and intermolecular correlations in colloids and polymers. A significant feature of the LQD is that a broad range of Q (0.003 to 0.5 Å^{-1}) is measured in a single experiment without any changes to the physical configuration of the instrument.

The LQD requires an intense source of long-wavelength ("cold") neutrons. Therefore, a liquid-hydrogen moderator is used, which produces a

neutron spectrum that peaks at about 2.4 Å and has usable flux from 0.3 to 20 Å . A pair of single-aperture collimator plates yields an angular resolution of 0.09° and a penumbra diameter of 10 mm at the sample. An optional five-hole-aperture converging collimator allows a four times increase in intensity without affecting the resolution.

At 20 Hz , the slowest neutrons used on the LQD fall 12 mm under the influence of gravity. Rather than increasing the size of the beam stop, neutrons whose parabolic trajectories strike the detector at its center are selected. The gravity-focusing device accomplishes this task by pushing the collimator exit plate upward at constant acceleration during each beam pulse.

Instrument Details

Wavelength range, λ	0.2 - 15 Å at 20 Hz	
Scattering angle	6 - 60 mrad	
Q range	0.003 - 0.5 Å ⁻¹	
Sample size:		
Single-aperture collimator	10 mm x 13 mm	
Multiple-aperture collimator	24 mm x 27 mm	
Detected intensity		
(single aperture, 30 μA):	0.2 < λ < 1.6 Å:	0.2 x 10 ⁴ n/s
	1.6 < λ < 5.0 Å:	8.0 x 10 ⁴ n/s
	5.0 < λ < 15 Å:	2.0 x 10 ⁴ n/s
Detector	1 multiwire, 59 cm in diameter	
Moderator	Liquid hydrogen at 20 K	
Sample environment	Air, vacuum, closed-cycle refrigerator, or user supplied	
Experiment duration	10 minutes to 12 hours	

Philip A. Seeger, instrument scientist
Rex P. Hjelm, Jr., instrument scientist
Dennis Martinez, instrument technician

LQD Experiment reports

5023	<i>Phase Transitions in Side Chain Liquid Polymers</i>	110
5049	<i>Morphology of Thermoreversible Atactic Polystyrene Around the Gel Point</i>	112
5058	<i>Troponin C/Troponin I Complex</i>	114
5103	<i>Characterization of Polymer Molecules at Interfaces by Small-Angle Neutron Scattering</i>	116
5071	<i>Inelastic Scattering Effects in TOF SANS</i>	117
5108	<i>SANS on Disordered Copolymers</i>	120
5140	<i>Phase Behaviour of Non-Ionic Microemulsions</i>	122
5148	<i>In Plane SANS from Thin Films</i>	128
5151	<i>SANS Study of Bicontinuous Microemulsions</i>	130
5404	<i>Observation of Voids in Aged ^{239}Pu δ-Phase Samples by Small-Angle Neutron Scattering</i>	132

Instrument used: <i>(please type)</i> Low-Q Diffractometer	Local contact: Dr. Thomas P. Rieker	Proposal number: <i>(for LANSCE use only)</i> 5023
Title: Phase Transitions in Side Chain Liquid Polymers		Report received: <i>(for LANSCE use only)</i> 2/8/93
Authors and affiliations: Joseph T. Mang and Satyendra Kumar Department of Physics and Liquid Crystal Institute Kent State University, Kent, Ohio 44242 and T. P. Rieker Advanced Materials Laboratory 1001 University Blvd. S.E., Suite 100, Rm 126 Albuquerque, NM 87106		
Experiment report: <p>The side chain polymer liquid crystal molecules (SCPLC) are composed of a long flexible polymer main chain with small, somewhat rigid molecules, known as side chains, attached to it by an alkyl linkage group (spacer). Interaction of these three, in the different liquid crystalline phases exhibited by the SCPLC, determines the overall conformation of the polymer main chain. In the isotropic phase (I), the side chains are randomly oriented. Upon cooling into the nematic (N) phase, the side chains become orientational ordered. Further cooling leads to the smectic-A (Sm-A) phase, which possesses one dimensional positional order along the long axis of the side chain. The N to Sm-A phase transition has been well studied in thermotropic monomer liquid crystals and although it is the simplest form of melting, it is still not completely understood.</p> <p>In the SCPLC's, the development of the orientational order of the nematic phase partially restricts the motion of the polymer main chain, thus distorting the spherical conformation found in the I phase. Depending on the microscopic interactions, the conformation becomes either oblate or prolate. In the Sm-A phase, because the side chains form well defined layers, the polymer main chain is expected to be confined at the interface of two smectic layers, making occasional hops between layers. The radius of gyration, $R_{ }$, of the main chain, parallel to the layer normal is expected to be smaller than the radius of gyration perpendicular, $R_{\perp}$, to this direction.</p> <p>We have studied the conformation of the polymer backbone in the N and Sm-A phases of two samples of poly(metha)acrylate (PMA-6-OCH₃) as a function of temperature. Each sample consisted of a mixture of partially deuterated (in the main chain) and non-deuterated PMA-6-OCH₃. The only difference between the samples was the amount of deuterated polymer. Sample #1 contained 75% deuterated polymer while sample #2 contained 50%. Each sample was aligned, by cooling into the Sm-A phase, in the presence of a 4 Tesla magnetic field. Line shapes for both samples are shown in figure 1. From these plots, it appears that the conformation of the</p>		

Experiment report (continued):

Figure 1. Line shapes obtained for the 75% (a) and 50% (b) deuterated samples in the Sm-A and N phases. In the Sm-A phase, the curves appear anisotropic, while in the N phase, the anisotropy is much reduced.

polymer main chain is anisotropic in the N and Sm-A phases and that this anisotropy is temperature dependent. Currently, the data is being analysed using Ornstein-Zernike and Debye-Bueche models, in order to obtain specific values for the radii of gyration.

The LANSCE facility is well suited for this experiment because data can be collected over a wide q -range, allowing one to gather high- q information pertaining to the degree and direction of the sample alignment in conjunction with the low- q information on main chain conformation.

References:

Instrument used: <i>(please type)</i> LQD	Local contact: P. Seeger LANSCE MS H805	Proposal number: <i>(for LANSCE use only)</i> 5049
Title: Morphology of thermoreversible atactic polystyrene around the gel point.		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: B. J. Olivier, LANSCE MS H805 P. Seeger, LANSCE MS H805 C.M. Sorensen, Kansas State University		
Experiment report: <p>The macroscopic properties of the gel state of matter are relatively well characterized when compared with their microscopic origins. Exactly what mechanisms are involved during the sol-to-gel transition is at this time is unclear although it is clear that physical versus chemical gelation processes are different. In addition, another transition exists below the gel temperature where the gel undergoes the so-called gel-to-"glass" transition. This is not a true glass transition in the sense that the system does not pass from an ergodic to non-ergodic state but rather the state remains non-ergodic. Furthermore, the system does not experience a sharp volume change when passing from this gel-to-glass-like state. It is best to refer to the state of the system as forming a gel-like glass. Not all gel systems experience this second transition.</p> <p>We have begun to study the structural properties of a thermoreversible, physical gel, in both of the above transition regimes. We have chosen atactic polystyrene(aPS) because it may undergo both transitions and also because of its ability to gel in a wide range of organic solvents, thus allowing us to maximize neutron contrast between the polymer and solvent. For this study, deuterated chains of atactic polystyrene were dissolved in carbon disulfide, acting as the solvent.</p>		

Experiment report (continued):

Small angle neutron scattering was done on aPS systems of different concentrations and different molecular weights as a function of temperature. With our cooling system, we could reach temperatures as low as 50K. Problems, however, resulted from these temperatures because the sample(quartz) cells could not handle the stress. An alternative sample(aluminum) cell was developed. Below are some of our results for $M_w=103k$ and $c=0.05g/cc$ (the semi-dilute regime).

References:

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
LQD	Phil Seeger	5058
Title: Troponin C/ Troponin I Complex EXP(5058)		Report received: (for LANSCE use only) 4/5/93
Authors and affiliations: Jill Trehwella Isotope Nuclear Chemistry Div. Los Alamos Natl. Lab. Glenn Allen Olah Isotope Nuclear Chemistry Div. Los Alamos Natl. Lab. Sue Rokop Isotope Nuclear Chemistry Div. Los Alamos Natl. Lab.		
Experiment report: <p>The troponin complex is found on thin filaments in muscle tissue. The complex includes troponin C (TnC), the component that binds Ca^{2+}, troponin T (TnT), the component bound to tropomyosin, and troponin I (TnI), the component bound to actin. Muscle contraction occurs when Ca^{2+} binds to TnC, inducing a structural change in the troponin complex. This structural change involves the release of the inhibition property of TnI upon the ATPase activity of actomyosin. This mechanism then allows the sliding of thick over thin filaments required for muscle contraction.</p> <p>Neutron scattering data have been measured for 78% deuterated TnC complexed with natural abundance TnI in the presence of Ca^{2+}. Measurements were performed at three different $\text{D}_2\text{O}/\text{H}_2\text{O}$ ratios in the solvent (i.e., 0, 0.4 and 1 ratios). Concentrations were approximately 5 mg/ml. Under physiological conditions the complex has a strong tendency to self-associate. The complex tends to self-associate to a larger extent when D_2O is present suggesting hydrophobic interactions are the dominant mechanism of association. High salt concentrations (2 M Urea) were used to minimize this association effect, however, this did not totally prevent association problems from occurring in the 100% D_2O sample. The 0% and 40% D_2O samples were determined to be monomeric in solution. The 100% D_2O sample was not further analyzed. X-ray scattering data was also measured for the complex in H_2O and combined with the neutron scattering data during analysis.</p> <p>From the known chemical composition of the sample, the scattering density match point of the complex was calculated to be $4.3 \times 10^{-10} \text{ cm}^2$. As shown in Fig. 1, this calculated match point together with the zero angle scattering of the neutron data have a linear dependence as expected.</p> <p>A Stuhrmann plot (R^2 versus $1/\Delta\rho$) for the combined neutron and X-ray data is shown in Fig. 2 (1). The negative slope of the data indicates that the higher scattering density component (TnC) is located more toward the inside of the complex. Three data points were not sufficient to determine whether the center of masses of the two components are coincident.</p> <p>At 40% D_2O in the solvent, the TnI components' contribution to the scattering is minimized and the signal is dominated by the TnC component. The</p>		

Experiment report (continued):

R_g value of 24 Å suggests that the TnC component remains extended when complexed with TnI and in the presence of Ca^{2+} . This result is different from that of the evolutionarily related and structurally similar calmodulin interacting with its target proteins like MLCK. In the latter case, calmodulin shows a contraction upon binding MLCK.

TABLE: Structural Parameters for TnC/TnI Complex from Guinier Analysis

$\% \text{D}_2\text{O}$	R_g (Å)	I_o (cm^{-1})	χ^2
0	26.3 ± 2.8	0.22 ± 0.03	1.2
40	24.0 ± 2.0	0.07 ± 0.02	0.8

Fig. 1: Dependence of forward neutron scatter for 78% deuterated TnC complexed with protonated TnI (in the presence of Ca^{2+}). Solid circles are from the neutron scattering data. The triangle is the expected match point as determined from the chemical composition of the system.

Fig. 2: R_g^2 versus $1/\Delta\rho$ (Stuhrmann plot) for 78% deuterated TnC/TnI complex in the presence of Ca^{2+} . $\rho = \rho_c - \rho_s$, where ρ is the mean scattering density of the complex and ρ_s the solvent scattering density. The two solid circles are from the neutron scattering measured on LQD at LANSCE and the triangle is from X-ray scattering.

References:

- (1) Ibel, K and Stuhrmann, H.B. (1975) J. Mol. Biol. 93, 255.

Instrument used: <i>(please type)</i> LQD	Local contact: Dr. R.P. Hjelm, Jr.	Proposal number: <i>(for LANSCE use only)</i> 5103
Title: CHARACTERIZATION OF POLYMER MOLECULES AT INTERFACES BY SMALL-ANGLE NEUTRON SCATTERING		Report received: <i>(for LANSCE use only)</i> 2/23/93
Authors and affiliations: W.C. Forsman and Peter Dreux Department of Chemical Engineering University of Pennsylvania Towne Building 220 S. 33rd Street Philadelphia, PA 19104-6393		
Experiment report: <p>The goal of this experiment was to use small-angle neutron scattering (SANS) to examine the conformation of polymer molecules confined to the solid-liquid interface in dispersions of finely divided particles. The polymer conformation is characterized by the <i>polymer density profile</i>, $\phi(Z)$, which is the volume fraction of polymer as a function of the distance Z from the surface of the particle.</p> <p>The work reported here is an extension of previous experiments on narrow molecular-weight-distribution poly(n-butyl methacrylate) chains chemically bonded (grafted) by one chain-end to nearly-monodisperse, 2300 Å SiO₂ spheres. Grafted and ungrafted spheres were dispersed in isopropanol (IPA). Experiments were done in mixtures of hydrogenous and deuterated IPA -- (HIPA and DIPA respectively).</p> <p>The interfacial polymers used in this work were di-block copolymers of non-adsorbing poly(n-butyl methacrylate) and adsorbing blocks of poly(dimethyl aminoethyl methacrylate). Molecular weights of the poly(n-butyl methacrylate) blocks were 37000, 53000 and 92000. Molecular weights of the adsorbing blocks were 35000, 23000 and 17000. Total molecular weights were 72000, 76000 and 109000. We arrived in Los Alamos with three sets of samples that we will classify as high-, intermediate-, and low-coverage in HIPA and DIPA. We had intended to study polymer density profile as a function of coverage and molecular weight of the non-adsorbing block.</p> <p>Unfortunately, the Los Alamos facility was plagued with safety and mechanical problems during the period of our visit. For all practical purposes, we got no new experimental data during this visit. We did, however, re-run some of the samples from our 1991 visit to clarify some ambiguities.</p> <p>Because of the problems encountered on our 1992 visit, our proposal for scattering during the 1993 cycle will be the same as last year.</p>		

Instrument Used: <i>(please type)</i> L Q D	Local Contact Rex P. Hjelm Jr./Phil A. Seeger	Proposal Number: <i>(for LANSCE Use Only)</i> 5071
Title: Inelastic Scattering Effects in TOF SANS		Report received: <i>(for LANSCE Use Only)</i> 4/9/93
Authors and affiliations: <u>Fabian Macias</u> LANSCE Rex P. Hjelm LANSCE Phil A. Seeger LANSCE P. Thiagarajan IPNS Division, Argon National Laboratory		
Experiment report: <h3>INTRODUCTION</h3> <p>The focus of this study is designed to measure qualitatively the inelastic, multiple and incoherent scattering contributions present for samples suspended in hydrogenous solvents when using time-of-flight small-angle neutron scattering techniques.</p> <p>A sample of uniform silica particles was chosen as the scatterer because of it has high scattering length density and is well characterized in size and shape. By systematically varying the ratio of solvent from purely protonated to deuterated, we can change the coherent cross section of the solvent (background) to match that of the silica and in turn see small deviations in the cross section from the hydrogen present in the solvent. Our ability to measure changes in the background is the basis of our understanding of elastic scattering although all other effects have not yet been characterized. If the silica were not uniform spheres, their surface deformations would interfere with the final results. Another phenomenon that hinders results in multicomponent systems is scattering from inhomogeneities within the individual particles which is reflected in the scattering amplitude A (ref 1).</p> <p>The other parameter varied for this study is the inclusion of high energy neutrons in the beam to excite librational modes within the solvent. At LANSCE, the Low-Q diffractometer is equipped with a 15 cm MgO filter that is used to remove high energy neutrons thus mitigating inelastic scattering contributions. Removal of the filter to include the epithermal neutrons allows measurements of deviations in the scattering cross section due to changes in beam energy.</p> <p>Understanding the magnitude of these changes in scattering cross section is very important to begin the development of a meaningful correction term that can be applied to weak or moderately weak scattering systems. It should be noted that this experiment had been attempted in 1990 but due to the failure of the hydrogen moderator only half of the experiment was completed (filter-in series). The 1990 filter-in series is being used as a reference model for the 1992 filter-in experiment.</p> <h3>MATERIALS and METHOD</h3> <p>Commercially available silica gel, Dupont's LUDOX HS-30, was prepared in varied ratios of ultra pure H₂O and 99.997% D₂O, and buffered to a pH of 7.60 with H₂O/NaOH. The HS-30 is a 30% silica stock solution and the particles were 12 nm in size</p>		

Experiment report (continued):

as characterized by the manufacture. The sample preparation involved diluting the stock solution to .9% W/V for the 0%, 19%, 39% and 78% deuterated samples. A 2.7% solution at 55% D₂O was prepared and measured but not used in the analysis because there is a concentration dependence of the scattering. (This measurement is still useful for another study of this system that investigates concentration dependence.) Finally, a .3% sample was prepared at 96% deuteration. Two scattering measurements on each of the samples were obtained, filter-in and filter-out.

Fluctuations in the background are probed through the method of *Contrast Variation*, utilizing changes of the hydrogen/deuterium of the solvent in which the silica is suspended. Plots of intensity versus contrast at fixed momentum transfer (Q) are used to extract terms corresponding to particle shape and distribution, to fluctuations within the particles, and to interference of these two contributions, all as a function of Q . This method of analysis has proven to be very versatile and effective in studies ranging from material science to biological studies.

RESULTS and DISCUSSION

Figure 1 A and B show the scattering intensity as a function of contrast for several values of Q , respectively for filter-in and filter-out. The lines are fitted parabolas, following the equation

$$I(Q) = \Delta\rho^2 I_{\Omega}(Q) + \Delta\rho I_{\Omega\zeta}(Q) + I_{\zeta}(Q)$$

Fitting this second order equation at each measured Q extracts the basic scattering functions. Figure 2 is the quadratic term of the equation and the major term in the overall scattering intensity. This term is referred to as the shape function. There is no significant difference in the shape function between filter-in and -out, but what can be seen is the difference in the shape of the curves between the 1990 data and 1992 data. The 1992 samples were 1/3 as concentrated as the 1990 samples, implying less particle-particle interaction, which produced the hump between .01 and .03 Å. Figure 3 is the internal scattering function and is the constant term. Although there are negative values in the intensity, which are meaningless quantitatively. Qualitatively, differences can be seen between the two scattering functions (filter-in and -out). It should be noted that no negative values for this function appear in the 1990 data. Figure 4 is the cross-term function and is harder to analyze. Within this function the shape and internal functions are convoluted. We have qualitatively seen the inelastic effects. The next logical step of this analysis is to quantitatively measure the inelastic effects present in time-of-flight neutron scattering.

1 A

1 B

Experiment report (continued):

2

3

4

References:

1. Rex P. Hjelm, Philip A. Seeger, and Wesley A. Wampler, Polymers and Polymer Composites, Vol. 1, No. 1, 1993

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
LQD	R.P. Hjelm/P.A. Seeger	5108
Title:		Report received: <i>(for LANSCE use only)</i>
SANS on Disordered Copolymers		2/23/93
Authors and affiliations:		
T.P. Russell and A.M. Mayes IBM ARC 650 Harry Road San Jose, California 95120		
Experiment <p>In lieu of some recent x-ray scattering experiments performed at the Stanford Synchrotron Radiation Laboratory, a series of neutron scattering studies were performed on LQD investigating the phase behavior of diblock copolymers of polystyrene and poly(n-butylmethacrylate), denoted P(S-b-BMA). The initial experiments proposed dealt with the investigation of the solution behavior of P(S-b-MMA) diblock copolymers. However, the importance of the studies on P(S-b-BMA) required this action.</p> <p>For all diblock copolymers studied to date one typically observes an order to disorder transition of the copolymer with heating. However, recent x-ray scattering results on P(S-b-BMA) showed that this diblock copolymer underwent the expected order to disorder transition but with further heating the copolymer ordered again. This most unusual behavior, which is analogous to the lower critical solution behavior of polymer blends, has never been observed previously. Neutron scattering studies were performed to elucidate the variation in the segmental interaction parameter, χ, as a function of temperature and molecular weight. The analysis of the results are not complete as of yet. However, several exciting results on the behavior of the scattering profile can be demonstrated at this time.</p> <p>Shown in Figure 1 is the scattering profile of the P(S-b-BMA) having $M_w = 6.8 \times 10^5$ as a function of temperature. The lowest profile was that obtained at 80°C. With heating, the scattering profile is seen to intensify and sharpen. Without question this results demonstrates that the copolymer is ordering with increasing temperature. Shown in Figure 2 is the peak intensity as a function of temperature for a heating and cooling run. What is evident is that the changes occurring on heating are fully reproducible and supports the fact that the copolymer is undergoing a thermodynamic phase transition. In addition, the increase in the intensity is clearly evident. Decreasing the molecular weight of the copolymer to 2.6×10^5 produced supporting data for this. At 60°C, the copolymer is disordered. The scattering profiles shown in Figure 3 are typical for a copolymer in the disordered state where the intensity is weak and the scattering is distributed in a broad maximum. However, upon heating, the scattering is seen to increase slightly with temperature. The intensity of the maximum in the profile</p>		

Ex is shown in Figure 4. Here, the intensity is seen to increase slightly with temperature. Even though the scatter in the data is larger, the trend is definitely clear. Experiments were also performed on a P(S-b-BMA) copolymer with $M_w = 9.9 \times 10^5$. However, the copolymer was never found to disorder over a temperature range from 90°C to 250°C.

Combining these results we are forced to draw the conclusion that this copolymer undergoes an order to disorder transition at lower temperatures and with increasing temperature reversibly re-orders. As the molecular weight of the copolymer is increased, the ODT increases and the DOT decreases such that, for the 9.9×10^5 copolymer, a disordered phase is never observed. These results clearly demonstrate that equation of state arguments must be used to describe the variation in χ with temperature. This is a significant new finding in the field of diblock copolymers and promises to open several new areas of research. We are currently in the process of determining χ and extending these studies further.

References:

Instrument used: <i>(please type)</i> LQD	Local contact: Phil Seeger	Proposal number: <i>(for LANSCE use only)</i> 5140
Title: Phase Behavior of Non-Ionic Microemulsions		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: Jess Wilcoxon, Organization 1153, Tony Martino, Organization 6211, Sandia National Labs, Albuquerque, N.M. PROPOSAL NUMBER: 5140		
Experiment report: Introduction <p>The purpose of this experiment was to learn more about the microstructure and interactions of inverse microemulsion systems. These systems consist of droplet-like structures with hydrophobic entities forming an interface with the majority oil phase, and an interior hydrophilic environment friendly to both water and electrolyte species (salts). We are particularly interested and motivated to investigate these systems since they provide excellent environments to carry out simple chemical reactions such as reduction and coprecipitation.¹⁻³ Examples of reactions which we have successfully executed using inverse microemulsions include formation of a wide range of useful metal sulfides such as FeS₂ (cubic pyrite), MoS₂, CdS and metal oxides such as Fe₃O₄. Nanosize clusters of these materials formed in inverse microemulsions have enormous technological importance, particularly in the areas of catalysis and photocatalysis. By investigating the initial size and interactions in several of these systems we hope to gain insight into the relationship between micelle size, polydispersity, interactions and final metal oxide or sulfide cluster size, shape, and polydispersity. This is a very ambitious goal in view of the large complexity inherent to these multicomponent systems, and makes interpretation of scattering data difficult. Our approach is to use both SANS measurements and static and dynamic light scattering to investigate structure, dynamics, and interactions on length scales from ~500 nm to ~1 nm.</p> Materials and Methods <p>The nonionic surfactant systems investigated had the generic formula CH₃(CH₂)_i(OCH₂CH₃)_jOH, which we abbreviate as C_iE_j in the following report. We also examined the effect of substitution of phenyl (C₆H₃OH) for methyl (CH₂) in the above surfactant system and we abbreviate these surfactants as Ph_iE_j in the following discussion. These surfactants allow one to adjust the phase behavior and microstructure by varying the ratio of hydrophilic (j value) to hydrophobic (i value) character of the molecule. The cationic surfactant, CTAB Hexadecyltrimethylammonium, CH₃(CH₂)₁₅N(CH₃)₃Br was investigated since it has an exceptionally large single phase microemulsion region when combined with an appropriate</p>		

Experiment report (continued):

In our previous report we examined the role of hydrocarbon chain length k on the microstructure of several $C_{12}E_4$ systems, in particular $C_{12}E_4$. We showed that each system formed inverse micelles and that the average size, as obtained from Guinier analysis of the SANS data increased from 22.9 to 31.2 Å as the k increased from 6 to 16. At the same time $I(0)$, which in the absence of interactions is proportional to the mass or aggregation number of the micelles, increases from 1.7 to 5.7 (arbitrary units). These two measurements are consistent with each other and imply a spherical micelle structure. However, the limiting slope at the largest values of Q available at LANSCH is -2, which is more consistent with a two-dimensional disc-like structure. However, this apparent slope may only be indicative of a slow cross-over to Porod law behavior. In fact, we favor this hypothesis.

In our first series of experiments we added water to several nonionic inverse micelle systems and examined changes in the scattering behavior. The changes we observed, even with very small amounts of added water, were quite dramatic as shown for the $C_{12}E_4$ /dodecane system of figure 1. Guinier analysis of the data of figure 1 results in the values of R_g and $I(0)$ shown. The approximate doubling in micelle size is not enough to account for the increase in $I(0)$ shown even assuming a spherical micelle structure, and so we must assume intermicelle interactions (phase boundaries) play an significant role in the changes observed.⁴ This is consistent with the observed phase separation that ensues when additional water is added to this system. Also, note the apparent change in limiting slope to Porod law behavior as expected for a droplet-like micelle with a sharp interface between the surfactant and the oil. This argues that the apparent slope of -2 shown in the figure is likely not the true limiting slope. This is due to the small mass of the bare micelles in these nonionic systems which means that the scattering intensity decreases below $I \sim 0.1 \text{ cm}^{-1}$ at high Q which appears to be the noise limit for LQD.

Continued on Attached Pages

References:

1. Wilcoxon, J. P., Baughman, R. J., and Williamson, R. L., *Formation of Catalysts in Inverse Micelles*, in Novel Methods for Catalyst Preparation, Symposium S, Proceedings of the Fall Meeting of the Materials Research Society, Boston, MA, Nov, (1990).
2. Wilcoxon, J.P., DOE patent #5,147,841, DOE control #S 70621, entitled "Method for the Preparation of Metal Colloids in Inverse Micelles and Product preferred by the method", issued Sep. 15, 1992.
3. DOE patent disclosure SD-5102 entitled, "Use of Highly Dispersed Materials as Coal Liquefaction Catalysts", submitted Feb 28, 1992, by Paul J. Nigrey, A.P. Sylwester, Jess P. Wilcoxon, Mark J. Hampden-Smith, and Zhibang Duan, assigned number SD-5102, S-75, 545.
4. Wilcoxon J.P., Critical Behavior of an Inverse Micelle System, *Phys Rev A*, 43, 1857, (1991).

Figure 1. The effect of addition of water to the C₁₂E₄/dodecane inverse micelle system is shown as a function of water weight fraction, ϕ_w .

As the hydrocarbon number k increases, the amount of water that can be solubilized without phase separation reaches a maximum at $k=12$. At this value of k the microstructural changes with water addition are quite striking (figure 1). In this system we are far enough from the phase boundaries after the first addition of water that the changes in R_g and $I(0)$ are consistent with an increase in average micelle droplet size with addition of water. The curve with $\phi_w=.025$ is obviously qualitatively different and must reflect the presence of the nearby phase boundary. In fact, very similar scattering is observed in the two phase region of the C₁₂E₄/hexadecane system with $\phi_w=.0107$ shown in a previous report. The importance of these observations is in emphasizing the role of nearby phase boundaries in the interpretation of the scattering data, even on these small length scales.

The cationic surfactant CTAB is interesting since it is not soluble in either water nor octane by itself, but in the presence of a cosurfactant such as hexanol, and a small amount of water forms transparent microemulsions in the region of water fraction $.02 < \phi_w < .27$. This is a very large region of stability for stable microstructures. Are the structures formed droplet-like and do they remain so as more water is added?

In a previous report we demonstrated that in the chemically similar cationic surfactant system, DDAB in dodecane, that addition of water leads

to tube-like (pseudo-one-dimensional) structures with intermediate scattering obeying $I \sim Q^{-1}$. The main difference in these two cationic systems is the presence of the cosurfactant in the CTAB system. This cosurfactant clearly has a profound effect on the evolution of the microstructure with added water as can be seen by comparing figure 2 of the present report with figure 3 of our previous report. As we will show, the cosurfactant alters the curvature and causes the system to remain droplet-like, with no hint of lower dimensional microstructures throughout the entire single-phase microemulsion region.

The scattering curves of figure 2 are consistent with a droplet-like microstructure throughout the single-phase region and the values of R_g and R_h (from dynamic light scattering) are consistent except for the first case of $\phi_w = .02$. We suggest that being so close to the phase boundary in this case affects the analysis of the Guinier regime (i.e. the intermicellar interactions must be taken into account). The limiting slope of -4 is also consistent with a droplet-like microstructure and a sharp oil-surfactant interface in each case.

Figure 2. SANS scattering data for the CTAB microemulsion system as a function of weight fraction ϕ_w water added. The system has 10 wt% hexanol, and 8.7% CTAB with deuterated octane as the continuous phase. The values of the hydrodynamic radius R_h (from dynamic light scattering), and the radius of gyration, R_g (from Guinier analysis of the SANS data) are also shown.

Upon changing the oil to hexadecane (C16) in the above system the regime for stability of droplet-like microemulsions shrinks somewhat to $.02 < \phi_w < .21$. Since the scattering contrast in the two fully deuterated systems is nearly the same the $I(0)$ values indicate an approximately 3x larger mass in the case of the hexadecane system. It is interesting to note that in the corresponding nonionic C12E4/C_k system we also observe around a 2-3 fold mass increase as k increases from 8 to 16.

We do not know whether the upturn in the data of figure 3 at low Q for the $\phi_w = .16$ system shown is real or due to instrumental difficulties. If it is real, then the Guinier analysis value of R_g is obviously invalid and the system scattering is probably being unduly influenced by the presence of the phase boundary at $\phi_w = .21$. Light scattering data supports the latter hypothesis as the addition of slightly more cosurfactant removes this feature, giving isotropic scattering at low Q . In fact, the changes in $I(0)$ observed in light scattering closely follow the changes shown in figure 3.

Figure 3. SANS scattering data for the CTAB microemulsion system as a function of weight fraction ϕ_w water added. The system has 10 wt% hexanol, and 8.7% CTAB with deuterated hexadecane as the continuous phase. The values of the hydrodynamic radius R_h (from dynamic light scattering), and the radius of gyration, R_g (from Guinier analysis of the SANS data) are also shown

This indicates that the scattering changes sufficiently far from the phase boundaries are mainly due to increases in the micelle average mass with addition of water. As in the case of the CTAB/octane system of figure 2, the scattering is consistent with a droplet-like microstructure.

Finally, it appears from light scattering measurements of R_h , that the microstructures are very small (i.e. $<20 \text{ \AA}$) at the lower extreme $\phi_w=.02$ of the microemulsion region. The fact that $R_g \gg R_h$ either implies that a significant fraction of the SANS scattering intensity is due to intermicelle interactions and that R_g should be interpreted as a correlation length in the solution or that the initial microstructure is not droplet-like, but becomes more so as the water weight fraction increases. The latter hypothesis is consistent with the fact that eventually $R_h > R_g$, consistent with a droplet-like microstructure at $\phi_w=.16$.

Instrument used: <i>(please type)</i> LQD	Local contact: R.P. Hjelm/P.A. Seeger	Proposal number: <i>(for LANSCE use only)</i> 5148
Title: In Plane SANS from Thin Films		Report received: <i>(for LANSCE use only)</i> 2/23/93
Authors and affiliations: T.P. Russell IBM ARC 650 Harry Road San Jose, California 95120		
Experiments Experiments were performed on LQD to determine the spatial distribution of polymer chains in thin films. In particular, mixtures of normal polystyrene ($M_w = 5 \times 10^6$) with perdeuterated polystyrene of similar molecular weight were prepared in toluene solution. Thin films ($\sim 200 \text{ \AA}$) of the mixture were spin coated onto fused silica substrates and floated off onto a pool of water. The films were retrieved using thin, rectangular quartz substrates such that the thin films were deposited onto both sides of the substrate. This process was repeated 25 times onto three separate substrates. The combined 150 layers of thin films were mounted into a goniometer designed to fit into LQD. The samples were then rotated in the beam such that the inclination of the sample with respect to the detector was 3° , 7° and 10° . In this way it intended to determine the radius of gyration of the polymer chains normal to and parallel to the surface of the film and, thereby, determine the extent of compression of the polymer chain due to the confinement in the thin film. <p>The results of the 3° experiment are shown below. The upper curve represents the scattering in a direction normal to the film surface whereas the lower curve is the scattering parallel to the film surface. The first major accomplishment of the experiments was that there was sufficient sample in the beam to resolve the scattering from the films and demonstrates that the experiments are feasible. However, extracting the single chain dimensions from the data could not be done reliably. This was not due to the performance of LQD but rather in a problem with the sample preparation. If the data normal to the film surface is examined a clear shoulder in the scattering profile is seen $q = 0.03 \text{ \AA}^{-1}$ which corresponds to $209 \text{ \AA}$. Such a scattering profile would not be expected from a gaussian coil, compressed or not. This distance corresponds to the thickness of the films which suggests that impurities entrapped between the films during the transfer process provided sufficient contrast to be detected. Consequently, the scattering observed normal to the film surface was contaminated with this artifact. There is no clear manner in which this contribution to the scattering can be removed. Consequently, these results suggest that a modification of the sample preparation is required to minimize the contamination entrapped between the layers. It should be noted that the origin of the contaminant is unclear at this present. One possible source is water entrapped between the layers. It is most difficult to remove this entrapped water without inducing some interdiffusion of the layers which would nullify the experiments. An alternative method of preparation is currently being pursued.</p>		

Experiment report (continued):

References:

Instrument used: (please type) L Q D	Local contact: R. Hjelm P. Seeger	Proposal number: (for LANSCE use only) 5151				
Title: SANS Study of Bicontinuous Microemulsions		Report received: (for LANSCE use only) 1/26/93				
Authors and affiliations:						
<table border="0"> <tr> <td>C. Toprakcioglu</td> <td>Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE</td> </tr> <tr> <td>P. Maddaford</td> <td>Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE</td> </tr> </table>			C. Toprakcioglu	Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE	P. Maddaford	Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE
C. Toprakcioglu	Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE					
P. Maddaford	Cavendish Laboratory Department of Physics University of Cambridge Madingley Road Cambridge, CB3 0HE					
Experiment report:						
<p>Numerous ternary surfactant systems with equal volume fractions of aqueous and hydrocarbon components have been shown to have a random bicontinuous microstructure. In such structures continuous domains of oil and water are separated by a randomly oriented monolayer of surfactant molecules. Small-Angle Neutron Scattering (SANS) measurements are particularly valuable in determining microemulsion structure, utilizing the contrast variation available in the technique to highlight different structural correlations.</p> <p>Recent theoretical work on the disordered bilayer structure of the L_3 "sponge" phase by Roux <i>et al</i>¹ can be extended to the special symmetric case of a monolayer structure when the two sub-volumes are exactly equal. This theory introduces a second order parameter in the Landau-Ginzberg approach which is associated with the symmetry of the system. This extra symmetry consideration introduces a second length scale ξ_h in addition to the usual one, ξ_p, associated with the density correlation function. The coupling of this second order parameter to the density order parameter is proposed to introduce a q^{-1} dependence for the scattered intensity at low q ca. $\leq 0.01 \text{ \AA}^{-1}$ instead of the well known q^{-2} Ornstein-Zernike form.</p> <p>Work by Kahlweit² on the ternary system consisting of the nonionic surfactant C_8E_3 /D_2O/Decane indicates that it has a fairly symmetric phase diagram at an experimentally convenient temperature range. Under carefully chosen experimental conditions it will satisfy the theoretical conditions to produce the unusual scattering behaviour mentioned above. With this aim a series of samples with $\phi_w \approx \phi_o$ to satisfy the symmetry considerations and varying surfactant content were prepared. The experimental temperature was set so as this surfactant dilution line intersected the tricritical point in the system. Under these conditions the surfactant sheets are expected to have zero mean curvature. The experiment was carried in both single and double deuteration mode so as to explore the validity of the Roux <i>et al</i> model.</p> <p>SANS profiles for the single deuteration case exhibit a characteristic peak in scattering intensity as previously observed³. The q-value of the maximum intensity varies with surfactant volume fraction and shows good agreement with the expected ϕ_s^{-1} behaviour (Figure 1). The position of the peak is indicative of the correlation length ξ_k of the surfactant film, a distance over which the film may be considered to be flat.</p> <p>SANS data for a double-deuterated sample is shown in Figure 2. The small peak in the intensity</p>						

Experiment report (continued):

appears in all samples and mimics the ϕ_s dependence of the peak in the single-deuterated case. The q -value of this peak has been proposed to be representative of a length scale relating to the most commonly occurring film-film distance within the structure⁴. The solid line in Figure 2 is the fit to the Roux model, and reasonable agreement can be seen to be achieved. Fits using the classical Ornstein-Zernike form for critical scattering gave a far inferior agreement. The improved fit for the Roux model seems to give a clear indication that the extra term in the theoretical scattering form is indeed valid. The value for $\xi_h = 4700 \text{ \AA}$ derived from the fit is in accord with results obtained from light scattering experiments on another system⁵.

Figure. 1 :- Plot of surfactant volume fraction (ϕ_s) versus q_m , the position of the correlation peak in the single deuteration experiment.

Fig. 2 :- SANS Profile of a sample with composition by weight of C₈E₃ : 25.0 %, D₂O : 37.5 %, d-Decane : 37.5 %. The solid line represents the fit to the Roux *et al* model.

References:

- (1) Roux, D.; Cates, M. E.; Olsson, U.; Ball, R. C.; Nallet, F.; Bellocq, A. M. *Europhysics Letters* **1990**, *11*, 229-234.
- (2) Kahlweit, M.; Strey, R.; Firman, P.; Haase, D. *Langmuir* **1985**, *1*, 281-288.
- (3) Auvray, L.; Cotton, J.-P.; Ober, R.; Taupin, C. *Journal of Physical Chemistry* **1984**, *88*, 4586-4589.
- (4) Schubert, K. V.; Strey, R. *Journal of Chemical Physics* **1991**, *95*, 8532-8545.
- (5) Roux, D.; Coulon, C.; Cates, M. E. *Journal of Physical Chemistry* **1992**, *96*, 4174-4187.

Instrument used: (please type) LQD	Local contact: P. A. Seeger	Proposal number: (for LANSCE use only) 5404
Title: Observation of Voids in Aged ^{239}Pu δ -Phase Samples by Small-Angle Neutron Scattering		Report received: (for LANSCE use only) 3/5/93
Authors and affiliations: <p>A. C. Lawson, T. G. Zocco, P. A. Seeger, R. Martinez, J. Cost and R. Hjelm, Los Alamos National Laboratory Los Alamos, NM 87545</p>		
Experiment report: <p>Self-irradiation damage of plutonium metal and its long term effects are of particular interest to plutonium metallurgists. With each radioactive decay event (α-decay), a helium nucleus and subsequent ^4He atom is formed, and over a long period of time these atoms can collectively add to a substantial amount of trapped helium in the lattice of the metal. It is important to know the distribution of trapped helium in order to predict its effects (e.g., swelling) on plutonium components.</p> <p>It is not known <i>a priori</i> what happens to the helium. One possibility is that it will form small bubbles, or voids, and these are sometimes seen with electron microscopy. Bubble formation can be influenced by heat treatment. We have examined three 27 year old samples of δ-phase plutonium by small-angle neutron scattering with the LQD at LANSCE. The samples are δ-phase, stabilized with 1.5 w/o gallium. Of our three samples, one was measured "as is," the second was heat treated at 250°C, the third at 400°C. We also examined a fourth, "new," sample that had received an identical heat treatment at 400°C.</p> <p>An intrinsic difficulty of this experiment is the high absorption cross section of ^{239}Pu. This means that very thin samples must be used, in our case 0.003". The samples were doubly contained in aluminum sample holders with windows of very high purity aluminum. The signal from the sample holders must be precisely subtracted. Accordingly, long measuring times are required. We tried for one full day on each sample and had to settle for somewhat less because of reliability problems. Even with the long measuring time, the precision of the data is limited by poor counting statistics at high Q.</p> <p>The data from these experiments are shown in Fig. 1. The points are shown with the error bars determined by counting statistics. The curves fitting these points were generated by fitting the data to a log-normal distribution of hypothetical helium voids ("pseudo-bubbles"). Mean pseudo-bubble diameters of about 60 Å are indicated. However, the fitting parameters are highly correlated, and these log-normal fits are considered to be unreliable, except for improving the appearance of the data. The important thing is that the data for the different samples - especially the new sample - are significantly different.</p> <p>We have attempted to invert these data to obtain the pseudo-bubble distributions unconstrained by the log-normal model. The results are shown in Fig. 2. There are intriguing differences in the distribution histograms in the 300-600 Å range, but these have very large error bars, and the differences may not be significant. An inversion procedure based on the maximum entropy technique would be much more reliable, and we are currently working on this. It is</p>		

Experiment report (continued):

Bubble distributions in delta Pu

already clear however, that the "new" sample does not match the others well enough to be used as a standard.

We have not yet been able to draw any firm conclusions on the possibility of bubble formation in ^{239}Pu on the basis of these experiments, but the implementation of the maximum entropy procedure should improve this situation. The fact that differences in the signals are observed at all is very encouraging, and we intend to continue these experiments with better samples.

References:

- D. L. Rohr, K. P. Staudhammer and K. A. Johnson, Los Alamos Report LA-9965-MS (1984)
- D. L. Rohr and K. P. Staudhammer, J. Nuclear Mat. 144 202 (1987).
- T. G. Zocco and D. L. Rohr, Mat. Res. Soc. Symp. Proc. 115 259 (1988).

RB 93036 007

*Surface Profile Analysis
Reflectometer (SPEAR)*

Surface Profile Analysis Reflectometer (SPEAR)

The Surface Profile Analysis Reflectometer (SPEAR) views a liquid-hydrogen moderator maintained at 20 K. The moderated neutrons are collimated into two beams within the bulk biological shielding of the LANSCE target. The beams are inclined downwards at angles of 1.5° and 1.0° to the horizontal and converge at a common sample position 8.73 m from the moderator. A specially designed mercury shutter allows the beams to be operated either independently or simultaneously. As defined by the in-shield collimation, the vertical resolution of each beam ($\Delta\theta/\theta$) is $\pm 5\%$ for horizontal surfaces, and the horizontal resolution ($\Delta\theta$) is $\pm 0.25^\circ$.

A " T_0 chopper" is located 5 m from the moderator in a heavily shielded cave just outside the bulk shield. This chopper rotates a 300-mm-long nickel slug into the beam during the initial flash of high-energy neutrons and gamma rays and significantly reduces the background that limits reflectivity measurements. At the midpoint of the beam line (6.19 m) is the frame-overlap chopper, which consists of a thin neutron-absorbing disc with two opposing 90° segments removed. Rotating at one half of the Proton Storage Ring (PSR) repetition rate, this chopper defines the wavelength band (1 to 16 Å or 16 to 32 Å) to be used and suppresses frame-overlap background problems between these frames.

A 2-m length of the beam path is accessible between the frame-overlap chopper and the sample position. This section allows for further tailoring of the incident beam. Modifications include slits for fine horizontal collimation of the beam for in-plane or diffuse scattering studies and polarizers for magnetic depth profile measurements.

A goniometer at the sample position allows solid samples to be tilted to change the angle of incident

of the beam relative to the reflecting surface. For the study of liquid surfaces, sample containers (e.g., Langmuir troughs) must be isolated from external sources of vibration. SPEAR uses an EVIS vibration isolation system (Newport Corporation), which supports the sample and actively dampens vibrations transmitted through the floor or air.

Two detector systems are available for use on SPEAR: a single ^3He detector for use in low reflectivity studies or a single linear position-sensitive detector with 1-mm resolution when high angular resolution is required for studies of off-specular scattering.

This year, LANSCE improved SPEAR by

- installing polarization analysis equipment;
- automating slit- and detector-position stepper motors, shutter, and chopper controls;
- installing a high-vacuum, *in situ* evaporation chamber for preparing nonoxidized metallic films; a Langmuir trough for studying liquid-vapor interfaces; and a flow cell for studying solid-liquid interfaces under shear; and
- improving the on-line database to include real-time display, black box versions of data reduction for instant examination, and data-space conversion routines.

A wide variety of support for users includes

- soft-wall and hard-wall clean rooms;
- a Millipore system to provide clean water for liquid samples;
- an automated Langmuir-Blodgett trough to prepare monolayer and multilayer films;
- an evaporator for deposition of metallic films as surface layers; and
- a surface ozone cleaner to remove organic contaminants.

Instrument Details

Moderator-to-detector distance	12.38 m
Wavelength frames at 20 Hz	$1 < \lambda < 16 \text{ \AA}$ $16 < \lambda < 32 \text{ \AA}$
Q range (horizontal sample)	$0.007 < Q < 0.3 \text{ \AA}^{-1}$
Beam cross section at sample position (maximum sample <u>acceptance</u>)	5-mm high x 50-mm wide (1° beam) 7.5-mm high x 50-mm wide (1.5° beam)
Moderator	Liquid H ₂ at 20 K

Neutron flux at sample position for 1.5° beam at 60 μ A:

$1 < \lambda < 6 \text{ \AA}$	$3.4 \times 10^5 \text{ n/cm}^2/\text{s}$
$6 < \lambda < 16 \text{ \AA}$	$3.3 \times 10^4 \text{ n/cm}^2/\text{s}$
$16 < \lambda < 32 \text{ \AA}$	$2 \times 10^2 \text{ n/cm}^2/\text{s}$

Detectors	Single ³ He tube 1-mm resolution linear ³ He position-sensitive detector
-----------	--

Minimum reflectivity	10^{-6}
----------------------	-----------

Typical run duration	30 min to 6 h
----------------------	---------------

Greg Smith, instrument scientist
Mike Fitzsimmons, instrument scientist
Ross Sanchez, instrument technician

SPEAR Experiment reports

5025	<i>Investigation of Structural and Interface Properties of Phthalocyanine-Based Thin Films on Liquid and Solid Supports by Neutron Reflectometry</i>	140
5026	<i>Investigation of the Surface Structure and Molecular Orientation of Newtonian and Non-Newtonian Fluids Under Shear Stress by Neutron Reflectometry</i>	144
5085	<i>Dynamics of Diblock Copolymers on Surface</i>	149
5038	<i>Interfacial Segregation Effects in Homopolymer-Copolymer Mixtures</i>	152
5081	<i>The Investigation of the Structure and Magnetic Properties of [001] Twist Grain Boundaries</i>	154
5084	<i>Random Copolymers at Homopolymer Interfaces</i>	156
5112	<i>Studies of the Magnetic Structure and Properties of Thin Films and Multilayers Grown In Situ</i>	158
5118	<i>Structure of (Poly)Ethylene Oxide Surfactants</i>	160
5155	<i>Neutron Reflectance Investigation of Block Copolymers at Interfaces</i>	162
5127	<i>Investigation of Boundary Effects on Highly Fluorinated Thermotropic Liquid Crystals by Neutron Reflectometry</i>	163
5137	<i>Do Surfactant Molecules Induce a Demagnetised Layer When Deposited on the Surface of Magnetic Materials?</i>	166
5411	<i>Characterization of Beta-Layers</i>	168
5700	<i>Structure of PDMS-PS Diblock Copolymer Monolayers at the Air Surface of Ethyl Benzoate</i>	170
5704	<i>Neutron Reflectivity Study of Diffusion in Amorphous Elemental Boron</i>	172
5138	<i>Wetting of Rough Surfaces</i>	174

Instrument used: <i>(please type)</i> SPEAR	Local contact: Shenda Baker	Proposal number: <i>(for LANSCE use only)</i> 5025
Title: Investigation of Structural and Interface Properties of Phthalocyanine-Based Thin Films on Liquid and Solid Supports by Neutron Reflectometry		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: Shenda Baker, Post -doc, LANSCE William Barger, Chemist, Naval Research Laboratory Art Snow, Chemist, Naval Research Laboratory		
Experiment report: <p>Introduction</p> <p>Phthalocyanine (Pc) thin films, their derivatives and multicomponent films are being developed for applications such as chemical sensors, fuel cell catalysts, sulphur effluent pollutant control and optical storage [1]. Metal chelated Pc's are semiconducting and can change conductivity by up to 6 orders of magnitude upon binding of certain gases. This conductivity is also sensitive to the orientation of the flat Pc rings relative to each other. The air/Pc or solid/Pc interface properties are as important as bulk properties in determining the device physical characteristics. Although the electronic and optical properties of these films have been studied extensively, the nature of the interaction of Pc films at the substrate, air or water interfaces is not well understood due to the paucity of applicable experimental techniques.</p> <p>Pc films are primarily prepared by the Langmuir-Blodgett (LB) technique. Monolayers are transferred from an aqueous layer to a substrate by successive dipping at constant film pressure/area. It is generally assumed the characteristics of the film on the aqueous phase will be retained upon the film transfer to the solid support but has not been difficult to prove. The effect of changing the physical characteristics (pH, T and impurities) of the aqueous layer supporting a substituted Pc indicates that the interaction between the Pc and water greatly affect the subsequent film deposition. Most substituted Pc's are hydrophobic and tend to form poor quality films unless amphiphilic transfer promoters are used. Whether the promoter and Pc are homogeneous or separate into microphases has not been determined, although conflicting data suggests that different mixed films have different relative tilt of the alkyl chains and Pc rings from perpendicular to flat stacked on the surface. [2]</p> <p>Neutron reflectometry allows for examining the same film before and after deposition from the liquid to the solid support; the assumed similarities between the film/solid and film/liquid can be addressed directly for the first time. Furthermore, the versatility of this technique can help to eliminate the controversy regarding the film density profile which has existed since the beginning of phthalocyanine and other thin film preparations. The extent of diffusion and interaction of the promoter at the interface with the Pc and the solid can be derived by using the contrast afforded by</p>		

Experiment report: (continued)

deuterium substitution of the promoter and by varying the promoter layer thickness. The relationship between the axis tilt angles of the Pc's and promoters can be then obtained with models using plausible molecular interactions to describe the density profile. The effects of varying pH, temperature and film pressures on the liquid/Pc interaction can then be addressed. Complementary studies with x-ray reflectometry and electron microscopy will help to characterize the film thickness and surface quality.

This research on SPEAR addresses two questions of related nature: what is the nature (structure) of the aqueous/pc/promoter film and interfaces and what is the nature of the resultant solid/promoter/Pc film and interfaces?

Experiment and Results

This year's efforts concentrated on understanding the packing and orientation of the film components at the solid/film interface. Thin films of tetrakis (cumylphenoxy) copper phthalocyanines with octadecanol as the transfer promoter were prepared on 2 inch polished silicon wafers as follows [3]: 1 monolayer (ML), 5ML, 9ML, 25ML with deuterated octadecanol and the same with hydrogenated octadecanol. Each sample was examined by neutron reflectometry, and information from specular and off-specular scattering was obtained.

Preliminary analysis of the reflectivity data indicates that the fits are not simple single-layers of homogenous octadecanol and substituted phthalocyanine. Incorporating the known "islanding" of the Pc's produces better fits, but a consistent model has not yet been determined. By comparing the data from the H- and D-octadecanol, which should be identical in number density but very different in scattering density, the potentially large number of "good fits" will be limited to that which fits both sets of data. **Figures 1 and 2** show only the reduced specular reflectivity data from this year.

Using the data from well controlled film transfer, x-ray reflectivity, EM and SPEAR:

-->specular reflection, the density profile can be obtained. Simulations of various Pc stacking patterns on silicon (parallel, perpendicular, tilted 45°, flat stacked with stack axis tilted 45° and 30°) indicate that the resultant reflectivity profiles are quite different. The resultant thickness and orientation determined from SPEAR will be compared to those inferred from the deposition parameters (amount of material per given surface area). The comparison of deuterated vs hydrogenated samples will help elucidate the location and effect of the transfer promoter. Comparison of the series of 1 to 25 monolayers (ML) will allow for the development of a model for film growth, changes in homogeneity and morphology, as the number of layers increases.

-->from diffuse scattering, the nature of the surface roughness may be studied. By establishing the surface roughness with TEM or EM, the roughness correlation between layers (or at least between the surface and substrate) can be determined. Furthermore, the known island formation in thicker films will provide very useful samples with measured roughness for the comparison of diffuse scattering to theory.

These results could have an impact on theoretical modeling of the electrical and optical properties of these films and on future deposition parameters of LB films in general.

Future Work

A Langmuir trough, developed during FY92 to facilitate reflectometry studies of films on liquid surfaces, will be used for the Pc/liquid interface to examine the same pressures and conditions used to deposit the thin films. Alterations to the aqueous properties will then be considered. A similar set of experiments of the film/solid monolayers is also planned, but with different transfer promoters

Figure 1 shows the normalized specular reflectivity *versus* q (perpendicular neutron momentum transfer) for a series of octadecanol (hydrogenated): tetrakis(cumylphenoxy) copper phthalocyanine, deposited in a 1:1 ratio. (square=1ML, triangle=5ML, plus sign=9ML, and asterisk=25ML). As the film thickness increases, the reflectivity tends to fall off more quickly. This fall off is expected and a result of the increased incoherent scattering due to the hydrogen in the sample.

Figure 2 shows the normalized reflectivity *versus* q for the same materials, the only difference being that the octadecanol is now fully deuterated. Symbols are the same as in Figure 1. Notice that the specular reflection does not fall off more rapidly with the thicker films. Also, the 25ML sample has a significantly shifted critical edge due to the thick deuterated layer close to the silicon surface. Most of the information for the thinner films is contained at the higher q values. Diffuse scattering was observed in both of the 25ML samples and to a lesser extent in the other samples (not shown here).

Experiment report (continued):

in order to understand the effects promoter properties on the resultant film. In this manner, the effect of the transfer promoter, liquid phase and film transfer on film morphology can be examined.

References:

- [1] C. Leznoff and A. Lever, eds. Phthalocyanines: Properties and Applications (VCH Publishers: NY), 1989
- [2] W. Barger, J. Dote, M. Klusty, R. Mowery, R. Price and A. Snow *Thin Solid Films* **159** (1988), p. 369
- [3] Detailed information on the LB deposition can be obtained from either W. Barger or S. Baker.

Instrument used: <i>(please type)</i> SPEAR	Local contact: Shenda Baker	Proposal number: <i>(for LANSCE use only)</i> 5026
Title: Investigation of the Surface Structure and Molecular Orientation of Newtonian and Non-Newtonian Fluids Under Shear Stress by Neutron Reflectometry		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: Shenda Baker, LANSCE Bill Hamilton, ORNL Paul Butler, U. Tennessee John Hayter, ORNL Greg Smith, LANSCE Lee Magid, U. Kentucky, U. Tennessee		
Experiment report: Introduction <p>The complex behaviour of non-Newtonian fluids is not well understood, although their properties are widely exploited in many industrial processes and products. Whereas Newtonian fluids experience a stress that is directly proportional to the strain independent of the strain rate, a non-Newtonian fluid under stress may store some of the energy input as molecular ordering rather than dissipating the heat. Some deformations may have a very long relaxation time so that the effect of a shear stress may be measured hours later. The viscosity of non-Newtonian fluids varies significantly with the applied shear rate as well and can have useful lubrication properties.</p> <p>Understanding the molecular interactions and orientations causing these marked differences in such fluids is beginning to emerge with the use of light scattering¹ and small angle neutron scattering (SANS) measurements^{2,3}. By subjecting the fluid to a velocity gradient, the molecular orientation in a fluid subject to a shear can be examined. We have used a parallel plate shear cell with continuous Poiseuille flow. Figure 1 Solutions at 20mM of hexadecyltrimethylammonium dichlorobenzoate were prepared—the 2,6 isomer being Newtonian and the 3,5 isomer being non-Newtonian. A NaCl solution of the 3,5 fluid and a 3,5 dichlorobenzoate salt (bromide) with a dodecyl (C-12 chain length) trimethylammonium were also prepared. Having the same mass density, but very different fluid properties, the 2,6 and 3,5 isomers provide a remarkable system to compare the ordering of non- and Newtonian fluids.</p> <p>In 1991, results from SPEAR suggested not only that differences exist between the Newtonian and non-Newtonian fluid density profile, but that these are significant and measurable quantities⁴. Each fluid 20mM was placed trough beneath a static quartz cover. The non-Newtonian fluid surface was subject to a shear stress by displacing the quartz cover along the beam direction. No difference was observed between the "sheared" and unsheared non-Newtonian fluid; however, the shear stresses from such a geometry would be very small and would require a very long relaxation time to be observed. With the construction of a dyanamic, parallel plate shear cell , this year we could apply a large range of continuous shear rates at low velocity in a geometry suitable for neutron reflection.</p>		

Experiment report: (continued)

Results

The 1992 research addressed the following questions:

1. **Differences in molecular orientation between non- and Newtonian fluids.** Is there a difference in the molecular orientation of a Newtonian fluid (2,6 compound) versus the non-Newtonian fluid (3,5 compound) when the fluids are not subject to a shear? A 20mM solution each of the 2,6 and 3,5 compounds were prepared in D₂O. Figure 2 shows the static results for the 2,6 and 3,5 compounds. The reflectivity is nearly identical for the range of q examined. Thus, the surface or near surface alignment (or lack thereof) of the 2,6 and 3,5 appear similar before shearing. Similar static reflectivity curves were also observed immediately after shearing indicating that the relaxation time is small compared to the time of data acquisition (1-4 hours).

2. **Molecular orientation of non-Newtonian fluids subject to a shear stress.** We can detect an ordering of molecules at the surface of the fluid subject to shear stress rates at all rates used (almost 2 orders of magnitude). The 3,5 fluid showed quite remarkable differences between the sheared and non-sheared fluids [Figure 3]. As the shear rate was increased, the peak did not significantly shift and grew only about 20%. However, due to the steep velocity gradient thought to be present at the surface of the quartz, the lowest velocity used may have already been well beyond the range of shear where alignment is just beginning.

The reflectivity of the sheared 2,6 fluid at all shear rates was identical to the static 2,6 and 3,5 fluids. [Figure 4] Note that the shear rates cited are calculated from the average velocity in the cell to give a relative comparison and may not be as large as the actual value. The cell was rotated 90° to allow for analysis of anisotropy parallel and perpendicular to the fluid velocity. For the static and a selection of shear rates at flow perpendicular to beam direction, the reflectivity curves of the 2,6 were identical to those at flow parallel to the beam. (3,5 was not done perpendicular)

3. **Effect of Salt and Different Chain Lengths on molecular orientation** Since molecular interactions are responsible for the 3,5 fluid's non-Newtonian properties, an attempt was made to change these interactions. First, to a new 20mM 3,5 solution was added .2M NaCl. The results are shown in Figure 5 Since no peak was observed, the salt apparently disrupted the interactions responsible for producing the surface layering or ordering. This effect is expected since the salt should screen the long range interactions.

A smaller chain of 12 rather than 16 carbons attached to the trimethyl ammonium 3,5 dichlorobenzoate would have a slightly different intermolecular interaction and different length scales. A comparison of the sheared 3,5 compound with the 12 C and 16 C chain is shown in Figure 6. Clearly, the obvious surface ordering or layering is again removed. However, it is not possible to conclude that *no* ordering has occurred since the length scale may just have been shifted beyond our measurable q range.

4. **Analysis of density profiles.** The modelling parameters of the fluid flow are important in determining the density profile. The parabolic velocity profile between parallel plates is well established for a Newtonian fluid, and thus is the shear profile. However, a non-Newtonian fluid has a much more complicated velocity profile which is not straightforward to calculate. Surfactants, such as those studied here, are of particular interest because of their lubricating properties, primarily due to some surface interaction. Theoretical calculations⁵ indicate that the shear is quite large at the walls of the cell, but decreases rapidly as the distance away from the wall. The bulk of the fluid moves through the orifice in a mass of constant velocity for a large class of non-Newtonian fluids with similar properties to those used here.. The molecular alignment occurs at the surface where the shear is greatest. We are presently in the process of performing anemometry (flow visualization to measure the velocity profile) and using the properties of similar viscoelastic materials to theoretically model the constitutive equations determining shear as a function of velocity profile. These experiments and calculations serve as a guide for our density profile models.

Experiment report: (continued)

Discussion and Future Work

The observation of a correlated length scale of the 3,5 fluid at high shear rates is not inconsistent with the SANS data recently analyzed of these materials⁶. While the SANS data showed a continuum of correlation lengths as the shear was increased, we did not observe a shift in the reflectivity peak. As mentioned before, it is likely that our range of shear rates was not sufficient to induce these changes. Future plans include a new cell and/or a new pumping system to allow for lower shear rates.

SANS data of the 2,6 fluid are scheduled for February (at NIST) and analyses of the SPEAR data and velocity profiles are ongoing.

Figure 1: Sketch of the shear cell used in reflectometry. The fluid outlets are on the ends and the tubing and pump are not shown. Fluid reservoirs are shown in black.

Figure 2: Graph of reflectivity as a function of momentum transfer (q) for the unsheared (static) 3,5 (asterisk) and 2,6 (diamond) fluids. Notice that they are nearly identical.

Experiment report (continued)

Figure 3: Graph of reflectivity as a function of momentum transfer (q) for the static 2,6 (diamond) and sheared 2,6 at 14/s (asterisk) and at 136/s (line) fluid. Notice that they, too, are nearly identical.

Figure 4: Graphs of reflectivity times q^4 as a function of momentum transfer (q) for the a) static (asterisk) and sheared (diamond) 3,5 fluid at 35/s and b) at <5 (plus) and ~35 (diamond) per sec. The peaks are more easily compared in this format.

Experiment report: (continued)

Figure 5: Graph of reflectivity as a function of momentum transfer (q) for the static 3,5 fluid (plus), static salt (diamond) and sheared salt (line) at 89/s.

Figure 6: Graph of reflectivity as a function of momentum transfer (q) for the static 3,5 16-carbon (plus), static 12-carbon 3,5 (diamond) and sheared at 68/s 3,5 12-carbon (line) fluids.

¹N. A. Clark and B. J. Ackerson *Phys. Rev. Lett.* 44, 1005 (1980)

²J. B. Hayter and J. Penfold *J. Phys. Chem* 88, 4589 (1984)

³P. H. Cummins, J. B. Hayter, J. Penfold and E. Staples *J. Chem. Soc. Faraday Trans. I* 83, 2773 (1987)

⁴G Smith LANSCE Exerimental Reports 1991

⁵D. S. Malkus, J. A. Nohel and B. J. Plohr *J. Comp. Phys.* 87, 464 (1990) and B. C. Eu *Am. J. Phys.* 58 (1), 83 (1990)

⁶Magid, Butler and Hayter Unpublished results

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
SPEAR	G. SMITH	5085
Title:		Report received: <i>(for LANSCE use only)</i>
Dynamics of Diblock Copolymers on Surfaces		
Authors and affiliations: <p>T.P. Russell, A.M. Mayes and P. Bassereau IBM ARC 650 Harry Road San Jose, California 95120</p>		
Experiment report: <p>Diblock copolymers are composed of two chemically dissimilar polymer chains covalently joined. In symmetric block copolymers the net repulsive interactions between the unlike monomers results in local segregation of the blocks and the formation of alternating lamellar nanocrystals of periodicity L which is a strong function of the copolymer molecular weight. If the copolymer is deposited as a thin film an orientational aspect is introduced to the ordering process since one block species will tend to interact preferentially with the free surface or the substrate. In this case the preferred orientation of the lamellae is parallel to the surface of the substrate. For this system the ordering kinetics is complicated by the effective field normal to the surface. The finite thickness constraint coupled with the orientation introduces a quantization of the film thickness to $(n+1/2)L$ or nL, depending on whether one block resides at one or both surfaces. For films which do not match the required thickness conditions as cast, holes (or islands) of depth (or height) L will form at the film surface to compensate for the lack (or excess) of material.</p> <p>The phenomenon of island formation has been studied previously by Coulon and coworkers [1,2] using Atomic Force Microscopy and optical microscopy. Their findings suggest that the island formation begins with a roughening of the surface which gradually evolves into two distinct film thicknesses. However, their surface studies reveal no information on how the ordering or orientation process within the film is coupled with the formation of surface features.</p> <p>In this study we followed the evolution of ordering in a thin copolymer film using x-ray and neutron reflectivity (NR) to reveal the ordering process and its connection to surface hole formation. Using an 80,000 mol. wt. poly(styrene-<i>b</i>-methyl methacrylate) copolymer with a fully deuterated styrene block provided ample contrast to examine the evolution of the ordered lamellae by neutron reflectivity. X-ray measurements, which are highly sensitive to the surface features of the films, were performed to investigate the surface roughness as a function of annealing time.</p> <p>Two sets of films were investigated: (1) a $2.5L$ system (800 Å) which forms no surface features and (2) a $>2L$ system (700 Å) with an equilibrium hole concentration of 30-40%. Multiple films of each thickness were spin cast on Si substrates from solution in toluene. Samples were annealed under vacuum at 170 ± 2 °C for times ranging from .1 hr to 24 hrs. Neutron reflectivity measurements were performed on the annealed and as-cast films on the</p>		

Experiment report (continued):

SPEAR instrument at the LANSCE facility of L.A.N.L. Specular and off-specular reflectivity data were collected simultaneously to q values up to $.12 \text{ \AA}^{-1}$. Sample runs were performed for approx. 3 hrs on each sample at a beam current of $70 \mu\text{A}$. X-ray reflectivity measurements were performed at the IBM Almaden Research Center on an 18 kW rotating anode instrument. X-ray measurements were taken out to $.25 \text{ \AA}^{-1}$ in q to enable sufficient characterization of the surface roughness.

Fits to the NR data of films in the as-cast state suggest that the systems had already segregated locally. In these films highly damped composition oscillations originating from the film surfaces were observed to have a periodicity of $\sim 1/3$ the equilibrium period. Transmission electron microscopy of thin as-cast copolymer films on gold confirmed these results, showing the entire film to display a quasiperiodic interconnected morphology. The large single layer oscillation observed at the Si surface in Fig. 1 suggests that the contact time of the solution to the substrate prior to the actual spinning is sufficient to allow the adsorption of a monolayer of copolymer to the Si surface. The as-cast films were found by x-ray reflectivity to exhibit extremely smooth free surfaces with an average roughness of several angstroms.

Upon annealing the characteristic period of the order in the film rapidly increases ($< .1$ hr) to reflect a value closer to that of the final period. At 170°C most of the organization and orientation of the domains is nearly completed within .5 hrs, as shown in Fig. 2 for the $700 \text{ \AA}$ film. At intermediate times the orientation process is observed to proceed from the substrate upward. The adsorbed copolymer layer thus creates a strong orientational field for nearby chains. The organization process is found to be essentially identical for both thicknesses during intermediate times. In each case the internal reorientation is accompanied by a substantial increase in the surface roughness to $\sim 40 \text{ \AA}$. For longer times the surface roughness of the $2.5L$ film decays as the morphology is fine tuned toward equilibrium. In the thinner film the formation of islands is observed to be a phenomenon primarily involving a reorganization of the uppermost layer of the copolymer, rather than one involving substantial interdiffusion with copolymers of the underlying layers.

References:

Fig. 1. $R(k)$ profile and fit for as-cast copolymer film

Fig. 2. $R(k)$ profile and fit for film annealed .5 hours.

1. G. Coulon, B. Collin, D. Ausserre, D. Chatenay and T.P. Russell, *J. Phys. Fr.* **52**, 2801 (1990).
2. B. Collin, D. Chatenay, G. Coulon, D. Ausserre and Y. Gallot, *Macromol.* **25**, 1621, (1992).

Instrument used: <i>(please type)</i> SPEAR	Local contact: G. Smith	Proposal number: <i>(for LANSCE use only)</i> 5038
Title: Interfacial Segregation Effects in Homopolymer-Copolymer Mixtures		Report received: <i>(for LANSCE use only)</i> 2/22/93
Authors and affiliations: <div style="display: flex; justify-content: space-between; margin-top: 10px;"> <div style="width: 30%;"> S. Anastasiadis C. Toprakcioglu G. Hadziioannou R. Gill </div> <div style="width: 65%;"> Foundation for Research and Technology-Hellas, P. O. Box 1527, Heraklion 71110, Crete, Greece. Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge, CB3 0HE, U.K. Polymer Chemistry Department, University of Groningen, Groningen, The Netherlands. </div> </div>		
Experiment report: <p>The structure of end-attached (tethered) diblock copolymer chains is of current theoretical interest in addition to its importance in a wide range of technological applications [1, 2]. Depending on the grafting density, σ, of such chains on a given interface, they can either exist as non-interacting (or weakly interacting) "mushrooms" (low σ), or strongly stretched "brushes" (high σ). The degree of stretching and hence the layer thickness also depend on the molecular weight (MW) of the polymer, and on the solvent quality. Theory predicts rather different segment density profiles and contrasting scaling behaviour for these two structures [3].</p> <p>In this project, our aim was to use Neutron Reflectometry methods to investigate the structure of d-polystyrene/poly(vinyl-2-pyridine (PS/PVP) diblock copolymers adsorbed onto silicon wafers from a matrix of unlabeled polystyrene (PS) homopolymer. These materials adsorb onto silicon via the PVP block, while the non-adsorbing PS block extends into the homopolymer matrix. In order to study the transition from brushes to mushrooms we used a series of diblock PS/PVP materials with a fixed PS molecular weight (75 K), but different MW values for the PVP block, which was varied from 3.4 K to 102 K. The PS homopolymer matrix had a MW of 184 K. Our results indicate a systematic trend as a function of PVP MW, the segment density profile becoming more "mushroom-like" (with a pronounced maximum in the profile) as the PVP block size is increased. We have used a Schultz function to model the scattering length density of mushrooms as described previously [4] (see Fig. 1). The results also show a decrease in the adsorbed layer thickness with increasing PVP MW, suggesting that the PS chains bearing larger PVP blocks are less stretched, since the mean distance between them is greater due to the larger area occupied on the surface by the PVP anchor. More detailed analysis of the data is currently in progress.</p>		

Experiment report (continued):

Preliminary measurements on the kinetics of adsorption and their effect on the interfacial structure were explored, but the attainment of equilibrium seemed to be too rapid on the time-scales and annealing temperatures used in our experiments. More Neutron Reflectometry work on the concentration and kinetic effects is planned, while parallel Nuclear Reaction Analysis experiments are currently in progress.

Figure 1. A) Neutron reflectivity profile and associated fit for the PS/PVP 75K/102K material, and B) Schultz function profile corresponding to the fit shown in (A).

References:

- 1) T. Witten, *Macromolecular Reports*, **A29**, 87, (1992).
- 2) A. Halperin, M. Tirrell, and T. Lodge, *Adv. Polym. Sci.*, **100**, 31, (1991).
- 3) K. R. Shull, *J. Chem Phys.*, **94**, 5723, (1991).
- 4) J. B. Field, C. Toprakcioglu, L. Dai, G. Hadziioannou, G. Smith, and W. Hamilton, *J. Phys. II (France)*, **2**, 2221, (1992).

Instrument Used: <i>(please type)</i> SPEAR	Local Contact M.R. Fitzsimmons	Proposal Number: <i>(for LANSCE Use Only)</i> 5081
Title: The Investigation of the Structure and Magnetic Properties of [001] Twist Grain Boundaries		Report received: <i>(for LANSCE Use Only)</i> 3/24/93
Authors and affiliations: E. Burkel (Sektion Physik, Uni Muenchen, Germany) J. Peisl (Sektion Physik, Uni Muenchen, Germany) M.R. Fitzsimmons (LANSCE) G.S. Smith (LANSCE)		
Experiment report: Using X-ray diffraction techniques, the atomic structure of twist grain boundaries can be deduced [1]. When applied to grain boundaries, these techniques are very time consuming and can have multiple interpretations. In many instances, only two parameters of a grain boundary are of any interest— its density and width, and so a less cumbersome technique other than X-ray diffraction, like neutron or X-ray reflection, might be useful in measuring these two grain boundary parameters. The purpose of this project was to determine the densities and widths of several different [001] twist grain boundaries. Since the density of a grain boundary differs from that of the bulk by 10% or so, the reflection of neutrons or X-rays from such an interface has a relatively small effect on the specular reflectivity compared to the sample surface. Furthermore, surfaces of evaporated films can be rough producing diffuse scattering, which may mask the diffusely scattered radiation from a grain boundary, if any. In order to enhance the reflectivity of the grain boundary and minimize diffuse scattering from the sample surface, we chose to make Ni bicrystals containing [001] twist grain boundaries by sintering together two single crystal thin-films— one of which was contrast matched to air. By mixing ^{62}Ni with normal Ni in the hearth of an e^- gun, we were able to reduce the scattering length density of the deposited film by more than 90% compared to that of normal Ni. We call these films contrast-matched films (Ni'). The Ni' films were epitaxially deposited on single-crystal NaCl, while conventional Ni films were epitaxially deposited on single-crystals of MgO. The two films were placed face-to-face, while still attached to their substrates, under uniaxial pressure and sintered at high temperature for a couple hours in vacuum. Prior to sintering, we exposed the slightly warm NaCl/Ni'/Ni/MgO sandwich to carbon-monoxide in order to reduce the native oxide that grows on the film surfaces during the transfer of the films from the deposition chamber to the furnace. After sintering, the NaCl substrate was dissolved in water. The bicrystal sample consisted of three reflecting interfaces— one that was only weakly reflecting at the sample surface, a second strongly reflecting grain boundary interface, and a third very smooth interface at the Ni/MgO phase boundary. Since the Ni/MgO interface was very smooth and the air/Ni' interface was only weakly reflecting, the diffuse scattering observed in Fig. 1, i.e. the intensity away from the condition where the angle of reflection equals the angle of incidence (corresponding to the bright stripe across the figure), arises largely from roughness of the grain boundary. Diffusely scattered radiation has also been observed in [001] twist grain boundaries of Au [2]. From the data in Fig. 1, the scattering length density of a grain boundary averaged over its lateral dimensions can be deduced; however, these data have not yet been analyzed.		

Experiment report (continued):

The reflectivity of the bicrystal sample was also examined with polarized neutrons. The purpose of this experiment was to measure the magnetization density profile of the bicrystal sample directly. The magnetization of a sample can be most easily demonstrated by comparing the ratio of the spin parallel reflectivity (neutron polarization parallel to the magnetization of the sample) to the spin anti-parallel reflectivity. This ratio is called the flipping ratio, and for a non-magnetic or anti-ferromagnetic sample is unity. The variation of the flipping ratio with momentum transfer, Q_z , normal to the surface of the Ni bicrystal is shown in Fig. 2. The sharp peaks are related to the magnetization of the entire bicrystal. Since a grain boundary is less dense than the bulk, the magnetization of the interface is expected to be larger than the bulk [3]. This enhancement might be observed as a larger flipping ratio; however, the decreased atomic density of a grain boundary, which is quantitatively known (in principle) from the unpolarized reflectivity measurements, might mask any change in the flipping ratio. If a change in the flipping ratio can be directly observed in the data, then we would expect to observe a long period modulation of this ratio with Q_z , corresponding to the thickness of the grain boundary (ca. 10 to 20 Å thick [1]). Such a modulation might be imagined in Fig. 2, but a measurement of the magnetization of the grain boundary requires further analysis.

Fig. 1 The specularly and diffusely scattered radiation plotted versus departure angle from the sample surface (α_f) and wavelength (λ).

Fig. 2 The flipping ratio measured for the Ni bicrystal with polarized neutrons.

References:

- [1] M.R. Fitzsimmons and S.L. Sass, *Acta Metall.*, **36**(12), 3103 (1988), M.R. Fitzsimmons and S.L. Sass, *Acta Metall.*, **37**(4), 1009 (1989).
- [2] M.R. Fitzsimmons and E. Burkel, accepted for publication in *PRB*.
- [3] J. Kubler, *Phys. Lett.*, **81A**(1), 81 (1981).

Instrument used: <i>(please type)</i> SPEAR	Local contact: G. Smith	Proposal number: <i>(for LANSCE use only)</i> 5084
Title: Random Copolymers at Homopolymer Interfaces		Report received: <i>(for LANSCE use only)</i> 2/23/93
Authors and affiliations: T.P. Russell and A.M. Mayes IBM ARC 650 Harry Road San Jose, California 95120		
<p>Ex: Adhesion at an interface between two immiscible homopolymers is typically limited by poor interpenetration of the dissimilar polymer chains. One possible method to improve the adhesive strength is by placing a copolymer at the interface, whereby the two copolymer components favor interactions with homopolymers on opposite sides of the interface. This has been demonstrated for a symmetric diblock copolymer of poly(styrene-<i>b</i>-methyl methacrylate) placed at an interface between PS and PMMA homopolymers. In this case, provided the thickness of the copolymer layer is below half its lamellar period, the copolymer organizes such that the PS block extends into the PS homopolymer and the PMMA block likewise interpenetrates with the PMMA homopolymer.</p> <p>While diblock copolymers hold promise as adhesion promoters, other studies suggest that more complex copolymer architectures, such as linear multiblock copolymers, may better reduce the interfacial tension and improve adhesion by effectively stitching together the homopolymers on opposite sides of the interface through looped block configurations which form a strong barrier to disentanglement. Random copolymers, while unlikely to show a strong tendency to organize at the interface, may nevertheless promote adhesion by serving as compatibilizing agents at the homopolymer/homopolymer interface. The present study examines a random PS-PMMA copolymer placed at an interface between PS and PMMA homopolymers to ascertain whether such copolymers hold potential as adhesion promoters.</p> <p>Thin films (30-200Å) of 1.6×10^5 molecular weight dPS-PMMA copolymer containing ~65 volume percent deuterated PS were sandwiched between 10^5 molecular weight homopolymers of PS and PMMA or dPS and PMMA. The trilayer structures were supported on polished Si substrates 5 cm in diameter and .25 cm thick, with the PMMA layer (2000Å) adjacent to the substrate and the PS layer (500Å) at the free surface. The films were annealed under vacuum at 170°C for several hours to allow local rearrangement of the polymer chains at the interface. Excessive annealing led to dewetting of the PS layer from the surface, a visual indication that the random copolymer did not substantially improve the interfacial adhesion.</p> <p>Neutron reflectivity measurements of the trilayer samples were performed on the SPEAR instrument at the LANSCE facility. For weak scattering systems (PS/Ran/PMMA) measurements were taken to $.06 \text{ Å}^{-1}$ in q while for strong scattering systems (dPS/Ran/PMMA) measurements were taken to $.10 \text{ Å}^{-1}$ in q. Typical</p>		

measurement times with the H⁺ beam running at 70 μ Amps were 1 and 3 hours for the strong and weak scattering systems, respectively.

Figure 1 is a typical result obtained for a weak scattering system with 100Å of random copolymer at the PS/PMMA interface. The reflectivity data is represented by open circles while the solid line indicates the fit obtained with the scattering length density profile inset in the upper right corner of the figure. As suggested in this profile the copolymer does not intermix substantially with the homopolymers. Instead it remains localized at the interface but relaxes to a spacial configuration more indicative of the copolymer radius of gyration in the melt. No evidence of organization at the interface is observed. However, the interface between the copolymer and the PS is always found to be sharper than that between the copolymer and the PMMA, suggesting that, although the fraction of PS in the copolymer is larger than that of PMMA, the copolymer mixes less favorably with polystyrene. This could reflect subtleties in the copolymer architecture which favor such an asymmetric copolymer configuration, or it may be a result of the slight repulsion known to exist between deuterated and hydrogenated polystyrene segments.

The conclusion that this random copolymer does little to improve the compatibility or interfacial strength at the PS/PMMA interface is further supported by the results in Figure 2, where 200Å of the random copolymer has been placed between dPS and PMMA. In the scattering length density profile inset the copolymer is again shown to remain essentially localized but not organized at the interface between the two homopolymers.

References:

Instrument Used: (please type) SPEAR	Local Contact M.R. Fitzsimmons	Proposal Number: (for LANSCE Use Only) 5112
Title: Studies of the Magnetic Structures and Properties of Thin Films and Multilayers Grown in situ		Report received: (for LANSCE Use Only) 3/24/93
Authors and affiliations: M.R. Fitzsimmons (LANSCE) M.A. Nastasi (LANL/MST-4) G.S. Smith (LANSCE)		
Experiment report: We examined the reflectivity of three thin-film samples with polarized neutrons. Each reflectivity profile generally consisted of measurements taken at two or three different angles of incidence. The angle of incidence was changed, since polarized neutrons at SPEAR are only available with wavelengths ranging from 2 to 8Å. During 1993, we plan to install transmission polarizing supermirrors, which we hope will extend the upper limit to 12Å. The measurements were taken with the spin flipper periodically turned off and on (with periods of ca. 5 and 10min., respectively) so as to reduce systematic errors that might appear during the one to two-hour-long measurements. The data was corrected for wavelength dependent variations in the efficiencies of the polarizer and spin flipper, using software available to SPEAR users, and reduced to provide reflectivity curves for the spin parallel, R_+ , and spin anti-parallel, R_- , states. In some cases (to be discussed), model structures have been simultaneously fitted to both reflectivity curves and used to deduce details about the magnetization density of the thin-films.		
1. Fe on MgO A thin-film of Fe was grown, <i>ex situ</i> , on a polished MgO substrate. X-ray diffraction measurements at grazing incidence taken at HASYLAB indicated that: <ul style="list-style-type: none"> • the Fe film was a single crystal, • the thickness of the Fe film was ca. 267Å, • the roughness of the air/Fe interface was correlated with that of the Fe/MgO phase boundary, • and a network of misfit dislocations (with period $\Lambda=105\text{\AA}$) existed in the Fe film at the Fe/MgO phase boundary. The observation of a structurally ordered phase boundary is significant, since phase boundaries like grain boundaries [1], are expected to be less dense than the bulk and might affect the magnetic moments of transition elements like Fe [2].		
The measured + and - reflectivities of the sample versus momentum transfer, Q_z , were compared to those for a model consisting of three different magnetic layers, representing the Fe film, and a nonmagnetic layer, representing the MgO substrate. Representations of the Fe film as one or two magnetic layers were investigated; however, these models could not fit the data at large Q_z . In our model, the scattering length density of the thin magnetic layer at the air/Fe interface corresponds		

Experiment report (continued):

to that of a 25Å thick layer of Fe₃O₄ or γ-Fe₂O₃ with an average magnetic moment of 1.6μ_B. The thickness of this layer is in good agreement with Mossbauer observations of similar films where layers of γ-Fe₂O₃ with thicknesses of between 10 and 30Å are reported [3]. The magnetic moment of this layer is only 70% of that expected for γ-Fe₂O₃ [4]. The bulk of the film consisted of a 208Å thick layer of Fe with a magnetic moment of 1.8μ_B or about 82% of the value reported in the literature [4]. The phase boundary was represented by a 29Å thick layer with only 66% the atomic density of Fe with an enhanced average magnetic moment of 2.5μ_B (an increase of 14% compared to bulk Fe). Self-consistent band structure for bcc Fe by Kubler [2] suggest the magnetic moments of Fe atoms may increase by up to 25% when the density of the material is decreased by 25% [2]. While the enhancement of the magnetic moment in the phase boundary that we observe is not as large as would be predicted by Kubler, it is, nevertheless, in qualitative agreement with his calculations.

2. Thin-films fabricated *in situ*

The primary purpose of this experiment was to examine the reflectivity of thin magnetic films deposited *in situ* with polarized neutrons. In the first experiment we were interested in comparing the reflectivity of an Fe film in its virgin state to that which containing a native oxide, i.e. the Fe/MgO sample. We were also interested in examining the magnetism of a thin Fe film as it became thinner, which can be, in principle, controlled by heating the sample to temperatures where the Fe/Si interface grows thicker as Si diffuses into the Fe film [5]. Unfortunately, the growth of the Fe₂Si layer occurred much faster than anticipated, forming a single non-magnetic layer of Fe₂Si in a matter of a couple minutes. We plan to repeat this experiment during 1993 using a heater/cryostat stage so that the sample can be quickly quenched and the growth of the Fe₂Si layer better controlled. Despite the difficulty in controlling the growth of Fe₂Si, we were able to measure the reflectivity of a non-oxidized Fe film.

In the second experiment, we decided to change the system from Fe to Ni anticipating better control over silicide growth, since the moving specie forming Ni₂Si is Ni [5], which is a larger atom than Si. In this experiment we were indeed able to control the growth of Ni₂Si and measure the magnetization of a thin Ni film as it grew thinner. Interestingly, we were unable to observe the complete transformation of Ni to Ni₂Si. Even after heating the sample to ca. 700°C for about 30 minutes, a thin Ni film, which was magnetic at room temperature, remained on the surface of the sample. While we were unable to accomplish the primary goal of this experiment— to measure the magnetization of ultra-thin-films, this interesting observation might be exploited during 1993 to observe the ferromagnetic-paramagnetic phase transformation of a thin Ni film and determine the ordering parameter of the transformation.

References:

- [1] M.R. Fitzsimmons and S.L. Sass, *Acta Metall.*, **36**(12), 3103 (1988), M.R. Fitzsimmons and S.L. Sass, *Acta Metall.*, **37**(4), 1009 (1989).
- [2] J. Kubler, *Phys. Lett.*, **81A**(1), 81 (1981).
- [3] T. Shinjo, T. Shigematsu, N. Hosorro, T. Iwasaki and T. Takada, *Jap. J. of Appl. Phys.*, **21**(4), L220 (1982); T. Shinjo, T. Iwasaki, T. Shigematsu and T. Takada, *Jap. J. of Appl. Phys.*, **23**(3), 283 (1984).
- [4] R.S. Tebble and D.J. Craik, *Magnetic Materials*, Wiley, New York (1969).
- [5] G. Ottaviani, *J. Vac. Sci. Technol.*, **16**(5), 1112 (1979).

Instrument Used: <i>(please type)</i> SPEAR	Local Contact Greg Smith	Proposal Number: <i>(for LANSCE Use Only)</i> 5118
Title: Structure of (Poly)Ethylene Oxide Surfactants		Report received: <i>(for LANSCE Use Only)</i> 4/6/93
Authors and affiliations: Greg smith, LANSCE, LANL Shenda Baker, LANSCE, LANL Xuan Liu, LANSCE, LANL Tonya Kuhl, University of California, Santa Barbara Jacob Israelachvili, University of California, Santa Barbara Suzie Steinberg, University of California, Santa Barbara Franz-Josef Schmitt, University of California, Santa Barbara Alan Berman, University of California, Santa Barbara Hisae Yoshizawa, University of California, Santa Barbara		
Experiment report: <p>There are a number of forces acting between molecules in complex fluid systems. Among them are the Van der Waals, hydration, electrostatic, undulation and peristaltic forces. The functional form of many of these forces has been studied using the force balance method^{1,2} in a large variety of systems. This method involves measuring the force as a function of separation between two opposing mica substrates onto which monolayers of the fluids have been adsorbed. There may or may not be an intervening layer of solvent between these monolayers. Although the functional forms of some forces have been measured, the mechanisms producing them are not well understood. For example, it has been argued that the hydration force is of entropic origin, arising from alignment of water molecules around head groups of complex molecules. An alternative explanation ascribes the hydration force to thermal excitations of individual molecules out of the plane of a layer of complex molecules (a protrusion force), causing a region of excluded volume between two interacting layers³. An understanding of the underlying mechanisms of the various forces will provide information essential to tailoring the macroscopic properties such as adhesion and lubrication.</p> <p>We are performing a systematic study of the structure of various complex fluids using neutron reflectometry. This technique yields information regarding the density profiles of layered materials perpendicular to their substrates and gives a measure of the average, instantaneous surface roughness.</p> <p>During the 1992 run cycle, we performed the first succesful series of experiments. We began by choosing a relatively simple system. We chose to study the density profile of a poly(ethylene-oxide) (PEO) surfactant at a solid-water interface. First, we constructed a quartz/silicon cell designed for these studies using the SPEAR instrument at LANSCE. Next the quartz/silicon was coated with chemically bound silane to make it hydrophobic. Then, the PEO surfactants were deposited on the quartz/silicon surface using the Langmuir-Blodgett technique. This allowed us to control the packing density of the molecules on the surface. Finally, the neutron reflectivity curves were measured. The neutron reflection results from the silicon substrate coated with a mixture of 1.5%, 5% and 10 % PEO mixed with DSPE are shown in Figure 1. We see clear differences between these three cases. We are currently in the process of analysing this data. As a guideline, we are using similar models to those which we</p>		

Experiment report (continued):

used to analyse an adsorbed polymer system onto quartz. The polymer work was done in collaboration with Dr. C. Toprakcioglu of Cambridge University. In that work, we found that two regimes existed in the density profiles⁴. The density profiles of the high surface coverage adsorbates were well described by the polymer "brush" theory of Milner Cates and Witten⁵; whereas, the polymer which adsorbed with a low surface coverage, had a "mushroom" type of surface density profile as predicted by the theory of Alexander and de Gennes^{6,7}. We are now in the process of applying these same theories to our various surface concentration regimes in the PEO surfactants.

References:

1. J. Marra and J. N. Israelachvili, *Biochem.*, **24**, 4608(1985).
2. Israelachvili, J.N. *Proc. Nat'l. Acad. Sci., USA*, **84**, 4722(1987).
3. J. M. Israelachvili and H. Wennerstrom, *J. Phys. Chem.*, **96**,520(1992).
4. J.B. Field, C. Toprakcioglu, L. Dai, G. Hadziioannou, G.S. Smith and W. A. Hamilton, *J. de Phys. II*, **2**, 2221(1992).
5. S.T. Milner, T.A. Witten, M.E. Cates, *Europhys. Lett.*, **5**,413(1988).
6. P. G. de Gennes, *J. Phys (Paris)*, **37**,1445(1976).
7. S. Alexander, *J. Phys. (Paris)*,**38**,983(1977).

Instrument Used: <i>(please type)</i> SPEAR	Local Contact G. Smith	Proposal Number: <i>(for LANSCE Use Only)</i> 5155
Title: Neutron Reflectance Investigation of Block Copolymers at Interfaces		Report received: <i>(for LANSCE Use Only)</i> 4/16/93
Authors and affiliations: DETERMINATION OF END-ADSORBED POLYMER DENSITY PROFILES BY NEUTRON REFLECTOMETRY. J. B. Field ¹ , C. Toprakciloglu ^{1,2} , R. C. Ball ¹ , H. Stanley ³ , L. Dai ¹ , W. Barford ⁴ , J. Penfold ⁴ , G. Smith ⁵ , and W. Hamilton ⁵ 1) Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, U. K. 2). AFRC—IFR—Norwich, Colney Lane, Norwich, NR4 7UA, U.K. 3). ICI, Colloid Science Group, The Heath, Runcorn, WA7 4QD, U.K. 4). Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, U. K. 5). LANSCE, Los Alamos National Laboratory, N. M. 87545, U. S. A.		
Experiment report: ABSTRACT. Neutron reflection techniques were employed to investigate the density profile of polystyrene/polyethylene oxide (PS/PEO) block copolymers adsorbed from d-toulene onto quartz. The geometry employed allowed the neutron beam to pass through the quartz substrate and be reflected from the quartz/d-toulene interface. The polymer chains are terminally attached to the quartz substrate via the PEO block, while the PS block does not adsorb thereby forming a polymer "brush." Our results are in good agreement with the layer thickness values determined by mica force balance measurements. The reflectivity profiles are well described by parabolic as well as error function density profiles normal to the interface, but the data cannot be fitted to exponential or power-law decay profiles. The molecular weight dependence of the layer thickness and adsorbance obtained from the data obey scaling laws in accord with the theory of polymer brushes. The above paper has been submitted to "Macromolecules."		

Instrument used: <i>(please type)</i> SPEAR	Local contact: Thomas Rieker / Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 5127						
Title: Investigation of Boundary Effects on Highly Fluorinated Thermotropic Liquid Crystals by Neutron Reflectometry		Report received: <i>(for LANSCE use only)</i> 3/8/93						
Authors and affiliations:								
<table border="0"> <tr> <td>T.P. Rieker</td> <td>LANSCE, Los Alamos National Lab, Los Alamos, NM 87545</td> </tr> <tr> <td>G.S. Smith</td> <td>LANSCE, Los Alamos National Lab, Los Alamos, NM 87545</td> </tr> <tr> <td>E.P. Janulis</td> <td>3M Co., Corporate Research Laboratories, St. Paul, MN 55144-1000</td> </tr> </table>			T.P. Rieker	LANSCE, Los Alamos National Lab, Los Alamos, NM 87545	G.S. Smith	LANSCE, Los Alamos National Lab, Los Alamos, NM 87545	E.P. Janulis	3M Co., Corporate Research Laboratories, St. Paul, MN 55144-1000
T.P. Rieker	LANSCE, Los Alamos National Lab, Los Alamos, NM 87545							
G.S. Smith	LANSCE, Los Alamos National Lab, Los Alamos, NM 87545							
E.P. Janulis	3M Co., Corporate Research Laboratories, St. Paul, MN 55144-1000							
<p>Experiment report: In this experiment we compared the molecular ordering in two thermotropic smectic liquid crystal by specular neutron relectometry. The homologs studied have the same structure except for the substitution of fluorine for hydrogen in one of the aliphatic tails, see Fig. 1. The fluorination of one of the aliphatic tails allows us to distinguish between a parallel or antiparallel alignment of neighboring molecules. We generate theoretical reflectivity curves from model molecular packings and compare the theoretical fits to the data.</p> <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;">a)</div> </div> <div style="display: flex; align-items: center; margin-top: 10px;"> <div style="margin-right: 10px;">b)</div> </div>								
<p>Figure 1 a) highly fluorinated and b) perhydrogenated homologs</p> <p>Thin unoriented samples were prepared by spin coating silicon wafers (cleaned with acetone) with solutions of liquid crystal dissolved in chloroform (1:10 by number). Homeotropically aligned smectic samples (smectic layers parallel to the plane of the substrate), a few 10's of layers thick, formed spontaneously as the samples were annealed at a temperature corresponding to the mid-point of the smectic A phase. In this phase the molecules are aligned normal to the smectic layers. Therefore, in this geometry we probe the neutron scattering length density along the length of the molecules.</p>								

In our preliminary analysis we considered two cases; 1) uniform layers with an average neutron scattering density (amorphous), Fig. 2 (a,b) and, 2) partitioning the smectic layer into one core and two tail regions. For the second case we considered parallel and antiparallel alignment of nearest neighbors for the partially fluorinated molecules, Fig 3 (a,b).

(a)

(b)

Figure 2 Uniform slab of average scattering length density on a silicon wafer a) highly fluorinated, and b) perhydrogenated liquid crystals. The points with error bars are the data while the smoother line is a fit to the above model.

(a)

(b)

Figure 3 Partitioning of smectic layer into one core and two tail regions for the highly fluorinated material with a) nearest neighbors aligned parallel, and b) antiparallel.

The model of a uniform slab of hydrocarbon is sufficient to explain the scattering observed for the perhydrogenated material as seen in Figure 2 (a). This is expected since this material has a nearly uniform scattering length density along the length of the molecule. This is clearly not the case for the highly fluorinated liquid crystal. Figure 3 indicates that in this material the nearest neighbor molecules are probably aligned parallel to one another. This we conclude is due to surface interactions which prefer either the fluorinated or perhydrogenated next to the substrate surface.

Future work will center on; 1) The development of more detailed models (expedited by interactive software currently under development at LANSCE). 2) The production of more uniform samples. 3) The characterization of samples using other techniques (optical microscopy, surface profilometry).

Instrument Used: (please type) SPEAR	Local Contact: G.S. Smith	Proposal Number: (for LANSCE Use Only) 5137
Title: Do surfactant molecules induce a demagnetized layer when deposited on the surface of magnetic materials?		Report received: (for LANSCE Use Only) 5/4/93
Authors and affiliations: X. Liu, M.R. Fitzsimmons, G.S. Smith, R. Pynn LANSCE, LANL, Los Alamos, NM 87544 D. Margulies, M. Carrey, A. Berkowitz CMRR, UCSD, La Jolla, CA 92093-0401		

Experiment report:

For nearly two decades, the unusual properties of ultrafine magnetic particles suspended in fluids containing organic surfactants have been studied [1,2,3,4]. These properties, which are of particular interest to industry, since organic coatings are used to protect magnetic storage device, include:

- Decreases in the saturation magnetizations of the particles.
- The surfaces of the particles were unresponsive to applied magnetic fields.
- Some particles, like NiFe_2O_4 , Fe_3O_4 , CoFe_2O_4 [5], exhibit enhanced magnetic hardness (very large coercivities) and are very anisotropic (shifted hysteresis loops) at cryogenic temperatures.

One explanation for these observations is that the surfactant may restrict or "pin" the alignment of magnetic moments on the surfaces of the particles. Pinning of the magnetic moments may result when locally strong and anisotropic electric fields are produced by the ionic bonding of surfactant molecules to the surfaces of particles. This pinning may produce a thin layer of material which is unresponsive to magnetic fields and, therefore, may appear to be demagnetized.

Alternatively, the unusual properties may be caused by the small sizes of the particles, which lead to alteration of their magnetic properties. For example, the spin density wave in bcc Cr can be suppressed by reducing its grain size to ca. 1 nm [6].

In order to determine whether the unusual properties of ferrite particles are due to the surfactant, which manifests itself as the surface to volume ratio increases, or due to small sizes of the ferrite particles, we have developed an experiment where the effect of a surfactant coating on a ferrite film can be directly observed. This experiment involves the measurement of the reflectivity of a ferrite (Fe_3O_4) film with polarized neutrons before and after coating with the surfactant stearic acid. If the surfactant changes the magnetic structure of the ferrite surface, then the reflectivity of the sample should change after coating. If, on the other hand, the magnetic structure of the film remains unchanged after coating, then we expect that the unusual properties observed in the ferrite particulate system are due to their small sizes. The Fe_3O_4 thin film was epitaxially deposited by reactive magnetron sputtering onto a polished $3.6 \times 5 \times 0.5 \text{ cm}^3$, $\langle 0001 \rangle$ $\alpha\text{-Al}_2\text{O}_3$ (sapphire) single-crystal substrate. Prior to deposition, the scattering length density ($\beta = 5.62 \times 10^{-6} \text{ \AA}^{-2}$) and surface roughness ($\sigma = 6.0 \text{ \AA}$) of the sapphire substrate were measured by neutron reflectometry. The Fe_3O_4 film thickness of $100 \text{ \AA}$ was measured using a Dektak machine (and confirmed with neutron reflection), and the stoichiometry of the film (Fe_3O_4) was determined with Mössbauer spectroscopy.

The reflectivity of the Fe_3O_4 thin film was measured using polarized neutrons provided by SPEAR. During the measurement a 1.2 T magnetic field was applied to the sample. The sample reflectivity was measured for momentum transfer perpendicular to the sample surface, Q_z , ranging from 0.01 to $0.15 \text{ \AA}^{-1}$. The ratio of the reflectivity curves taken with neutron polarization parallel and anti-parallel to the applied magnetic field, called the flipping ratio, is shown for the uncoated sample in Fig. 1 (o).

Experiment report (continued):

After these measurements were taken, the film was cleaned with ozone, and a monolayer of stearic acid deposited on the film using the Langmuir-Blodgett (LB) technique [7,8]. Stearic acid was chosen as the surfactant because:

- its neutron scattering length density is about the same as that of air, hence stearic acid is nearly transparent to neutrons,
- and stearic acid can be easily deposited as an ordered monolayer with the LB-technique.

The flipping ratio of the coated film, as shown in Fig. 1 (○), is significantly reduced at large Q_z compared to that of the uncoated film. This observation suggests that, qualitatively, the magnetization of the sample has been reduced by surfactant coating. A preliminary analysis suggests that a model structure with a 0.33% demagnetized surface layer, i.e. the magnetization of this layer was 0.66% of that of the film, 20Å thick can reproduce the data, as shown by the solid curves in Fig. 1.

Fig. 1 The flipping ratios of the uncoated (○) and coated (●) Fe₃O₄ film. The solid curve is a fit to the data of a model discussed in the text.

References:

- [1] R.Kaiser and G.Miskolczy, J. Appl. Phys, 41 1064 (1970).
- [2] A.Berkowitz and J.Lahut, in AIP Conf, Proc. 10, ed. by C. Graham and J. Rhyne, 996 (1973).
- [3] A.Berkowitz and et.al., Phys. Rev. Lett. 34, 594 (1975).
- [4] A.Berkowitz and et. al., IEEE Trans. Mag. Vol. Mag_16, No.2, 184 (1980).
- [5] R.Pynn and J.Hayter, Phys. Rev. Lett. 51, 710 (1983).
- [6] M.R. Fitzsimmons, J.A. Eastman, R.A. Robinson, A.C. Lawson, J.D. Thompson, R. Movshovich and J. Sati, submitted to PRB.
- [7] K.Blodgett and Irving Langmuir, Phys. Rev. Vol. 51, 964 (1937).
- [8] G.Gaines, Jr., Insoluble Monolayers at Liquid- Gas Interfaces, Wiley-Interscience (1966).

Instrument used: <i>(please type)</i> SPEAR	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 5411
Title: Characterization of Beta-Layers		Report received: <i>(for LANSCE use only)</i> 2/1/93
Authors and affiliations: J. K. Hoffer and R. J. Candler, P-10 M. Salazar and L. R. Foreman, MST-7		
Experiment report: Introduction Beta-layering is an effect whereby solid tritium, or a solid deuterium-tritium (DT) mixture, automatically redistributes itself into a uniform layer on the inside of the container walls. The driving force is the self-heating due to beta decay of tritium into ^3He . The redistribution occurs by sublimation/condensation at the solid-vapor interface, following an exponential rate constant $\tau \approx 30$ min. in 50-50 DT. The effect is noticeably slowed down by the presence of non-condensable ^3He in the vapor space. Beta-layering is the only known method of preparing a thick, symmetric layer of dense DT fusion fuel inside of inertial confinement fusion (ICF) targets, and is thus of great interest to the national ICF program. Shortly after solidifying, the normally transparent DT layer starts to become optically dark, due either to radiation damage or to the accumulation of finite-sized ^3He bubbles. The formation and morphology of these ^3He bubbles can be studied by neutron scattering experiments. Furthermore, neutron radiographs should reveal whether the ^3He remains locked in the solid or migrates to the central vapor space.		
Experiments During the 1992 LANSCE run cycle, an attempt was made on the SPEAR apparatus to radiograph a beta-layered ICF target. No ^3He accumulation was observed. However, the target was later found to contain <u>no</u> DT. The cylindrical sample cell had been filled (6000 psia) with 19.9 Ci of DT at EG&G Mound. The small "puff" of tritium detected when the shipping container was opened at Los Alamos was later determined (from readings of the effluent stack monitor) to be the entire inventory. Poor packaging had caused the sample to vibrate in shipment and a joint in the filling capillaries had ruptured, although this was not obvious when the target was mounted.		

Experiment report (continued):

A second target was obtained from Mound in time for an attempt to do SANS on the LQD. The target was unpacked at Los Alamos and mounted in a fixture. It was then left unattended inside a hood prior to mounting it in the cryostat in time for the experiment two days hence. Sometime during this period, causes unknown resulted in the fill capillaries being severely bent. During the attempt to straighten the capillaries so that the target could be mounted in the cryostat, a joint cracked and the tritium inventory was lost up the stack. An off-normal occurrence report was filed with DOE.

The root cause for both these misfortunes lies in the 20 Ci limit imposed by DOT for class-A shipping of tritium. This results in a very small inventory, which in our case translates to low sensitivity. Therefore, the target design is necessarily less robust than one designed for a larger inventory. For instance, in order for not more than 10% of the inventory to be captured in the filling capillaries following liquid condensation, the capillary ID must be approximately 0.005" or less.

Tritium Handling

The SOP for handling the DT-filled aluminum targets was followed during the course of our work. In spite of the releases, no tritium contamination occurred. The effluent stack monitor serving LANSCE has now been calibrated for tritium.

Further Work

We still believe that neutron experiments will contribute significantly to our understanding of the beta-layering process, and in spite of these disappointing results, we will attempt the experiments again. The targets are being redesigned to utilize more robust filling/pinch-off capillaries which hopefully will withstand the rigors of shipping, handling, and (heaven forbid!) mishandling.

References:

Instrument used: <i>(please type)</i> SPEAR	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 5700				
Title: Structure of PDMS-PS Diblock Copolymer Monolayers at the Air Surface of Ethyl Benzoate		Report received: <i>(for LANSCE use only)</i> 1/15/93				
Authors and affiliations:						
<table border="0"> <tr> <td>Michael S. Kent</td> <td>Sandia National Laboratories</td> </tr> <tr> <td>Greg Smith</td> <td>Los Alamos National Laboratories</td> </tr> </table>			Michael S. Kent	Sandia National Laboratories	Greg Smith	Los Alamos National Laboratories
Michael S. Kent	Sandia National Laboratories					
Greg Smith	Los Alamos National Laboratories					
Experiment report:						
<p>We have used neutron reflectivity to study the conformation of a PDMS-PS diblock copolymer (4.5k - 60k) spread as a monolayer on the surface of ethyl benzoate (EB). EB is a good solvent for PS and a nonsolvent for PDMS. PDMS homopolymer spreads to form an insoluble monolayer on the surface of EB. Since the copolymer also spreads on EB, the PDMS block is believed to lie flat on the surface while the PS block is submerged. The copolymer monolayer is spread by simply placing a dry grain on the EB surface. The PS block was fully deuterated while the PDMS block and EB were hydrogenated. Since the scattering length density of PDMS is nearly matched with air, only the PS block was observed.</p> <p>Previous measurements on the DESIR reflectometer (LLB, Saclay)¹ were limited to a range of $q (=4\pi\sin\theta/\lambda)$ up to $0.045 \text{ \AA}^{-1}$. While this range was adequate to obtain the large scale characteristics of the segmental concentration profile of the PS block, no information could be obtained regarding the finer details of the profile such as the presence of a depletion layer near the surface and an exponential tail-off far away from the surface. These details have been predicted theoretically,³ but experimental evidence so far has been scarce.² The presence of a depletion layer is important for the interpretation of the rapid rise in surface pressure with surface concentration which has been observed for the present system.¹ On SPEAR, the measurable range of q extended from the critical q of roughly $0.008 \text{ \AA}^{-1}$ up to $0.12 \text{ \AA}^{-1}$ by using both frames for the 1° beamline. This q range allowed a clear characterization of each of the above features.</p> <p>A representative reflectivity curve is shown in Figure 1 (surface pressure of 2.7 dyne/cm). The data are plotted as the reflectivity from the copolymer monolayer covered surface divided by that for the pure solvent surface. The reflectivity for the pure solvent agreed well with the Fresnel curve with 0 to 3 Å roughness. The solid curves are the best fits (minimization of chi-squared) obtained for the following PS segmental concentration profiles (shown in Figure 2): a parabolic profile with an exponential tail (1), a parabolic profile with a depletion layer (2), and a parabolic profile with both an exponential tail and a depletion layer (3). The experimental data fall below curve (1) for $q > 0.04 \text{ \AA}^{-1}$ indicating that a depletion layer is required to fit the data. The exponential tail is also required, as shown by the fact that curve 2 oscillates more than the experimental data,</p>						

Experiment report (continued):

particularly around $q = 0.02$ to $0.04 \text{ \AA}^{-1}$. Thus these data show conclusively that the concentration profile of the dangling PS blocks contains both a depletion layer near the surface and a smooth tail-off far away from the surface.

Figure 1. Reflectivity data compared with best fit curves from model profiles

Figure 2. Profiles corresponding to the curves in Figure 1

References:

1. Kent, M.S., Lee, L.T., Farnoux, B., Rondelez, F. *Macromolecules* **1992**, 25, 6240.
2. Field, J. B., Toprakcioglu, C., Ball, R.C., Stanley, H.B., Dai, L., Barford, W., Penfold, J., Smith, G., Hamilton, W. *Macromolecules* **1992**, 25, 434.
3. Muthukumar, M., Ho, J.S. *Macromolecules* **1989**, 22, 965.

Instrument Used: <i>(please type)</i> SPEAR	Local Contact Greg Smith	Proposal Number: <i>(for LANSCE Use Only)</i> 5704
Title: Neutron Reflectivity Study of Diffusion in Amorphous Elemental Boron		Report received: <i>(for LANSCE Use Only)</i> 4/1/93
Authors and affiliations: Gregory S. Smith, LANSCE Michael Nastasi, LANL Shenda Baker, LANSCE Kevin Hubbard, LANL		
Experiment report: <p>Amorphous ceramics are promising materials for passivation and protection of surfaces under extreme conditions of wear and corrosion. In particular, refractory materials of boron with group IVa and Va metals possess the desired properties of high strength, high melting temperature and corrosion resistance^{1,2}. Furthermore, when amorphous films of these materials are used, the embrittlement, lack of adhesion and grain boundary corrosion associated with polycrystalline forms of the same composition may be avoided. In this work, we begin a study of the diffusion of amorphous materials by studying the mutual diffusion in amorphous, thin bilayer, films of pure ^{10}B and pure ^{11}B.</p> <p>Although several techniques exist for the determination of diffusion constants from density profiles, each has its own limitations. For example, ion milling of radioactive materials and secondary ion mass spectroscopy (SIMS) destroy the samples as the measurements are being performed³. While Rutherford back scattering spectroscopy is harmless to the samples, the depth resolution is on the order of only $100\text{\AA}$³. All of these techniques lack the capability of measuring detailed, interface, density profiles because the high energy probes involved alter and smear the density profiles during the measurements. The large contrast between the neutron scattering lengths of chemically identical ^{10}B and ^{11}B allows the examination of the density profile between two diffusing films of elemental boron using neutron reflectometry. From this density profile, the diffusion constants can be determined.</p> <p>During the 1991 LANSCE run cycle, we performed a series of neutron reflectometry studies to investigate atomic diffusion in elemental boron. The samples used for the measurements were thin-film bilayer structures consisting of alternating layers of isotopically enriched ^{10}B and ^{11}B, deposited by electron-beam evaporation. The reflectometry studies were performed with a beam of pulsed neutrons having a broad thermal spectrum incident on the samples at an angle of $\sim 1.00^\circ$. Specularly reflected neutrons were detected as a function of their time-of-flight with a position-sensitive detector. This data was reduced to obtain a plot of the reflectivity vs. the perpendicular wavevector. Because of the different nuclear potentials for the two boron isotopes, an interference pattern was observed, analogous to those obtained by X-ray</p>		

Experiment report (continued):

measurements on samples with a modulated index of refraction. Reflectivity profiles were measured and analyzed as a function of annealing time for temperatures of 360°C and 400°C. Variations in the interference patterns were then used to determine the diffusion coefficient, D , at 360°C, and hence the intrinsic diffusion parameters. A typical equilibrium result was determined⁴ to be $D \sim 10^{-1} \text{ Å}^2/\text{s}$, measured at an annealing temperature of 360°C. These measured diffusion constants are inconsistent with the high melting temperature of elemental boron, but are consistent with measured diffusion constants in other amorphous thin films⁵.

The only physical model found to fit the data taken in 1991 included a discontinuity at the ^{10}B - ^{11}B interface rather than the expected error function form⁴. One explanation for this was that there had been an oxide layer deposited at that interface due to a 4 minute time lag between depositions of the two layers. Therefore, we prepared new samples in an evaporator with a shutter system to minimize the time delay. These samples were examined during the 1992 run cycle. The fits to the data are shown in Figure 1 and the resulting model profiles in figure 2. We see that again the discontinuous solution to Ficks laws is required to fit the data. We are presently examining the samples further to try to determine a reason for this behavior other than an oxide layer at the interface.

Figure 1

Figure 2

References:

1. D. Gupta, "Special Aspects of Diffusion in Metallic Thin Films," Mat. Res Soc. Sym. Proc., 47, pp 11-26, Materials Research Society, , 1985.
2. A. Kaloyeros, M. Hoffman, and M.S. Williams, "Amorphous Transition Metal Carbides," Thin Solid Films, 14, pp 237-250, 1986.
3. H.O. Pierson, and A.W. Mulendore, "Thick Boride Coatings by Chemical Vapor Deposition," Thin Solid Films, 95, pp 99-104, 1982.
4. G.S. Smith, W.A. Hamilton, M. Fitzsimmons, S. M. Baker, K.M. Hubbard, M. Nastasi, J-P. Hirvonen, and T Zocco, SPIE Proc., vol. 1738, "Neutron Optical Devices and Applications," Charles F. Majkrzak and James L. Wood eds., p 246(1992).
5. B. Cantor and R.W. Cahn, "Atomic Diffusion in Amorphous Alloys," Amorphous Metallic Alloys, ed. F.E. Luborsky, Butterworths, London, 1983.

Instrument used: <i>(please type)</i> SPEAR	Local contact: Shenda Baker	Proposal number: <i>(for LANSCE use only)</i> 5138
Title: Wetting of Rough Surfaces		Report received: <i>(for LANSCE use only)</i> 2/1/93
Authors and affiliations: Roger Pynn, LANSCE Shenda Baker, LANSCE Greg Smith, LANSCE		
Experiment report: <p>Understanding the effect of surface and interface roughness on the diffuse scattering in reflectometry experiments is imperative, not only for interpreting the diffuse scattering, but also for properly reducing the specular data. We have begun a program of examining rough surfaces and those same rough surfaces coated with a wetting fluid in order to compare experimental results with theory being developed at LANSCE [1] to fully describe diffuse scattering.</p> <p>Experimental Results</p> <p>A number of surfaces were examined prior to and after certain roughening techniques:</p> <ol style="list-style-type: none"> 1. Sapphire-two samples of sapphire were obtained with roughnesses measured to be 14 and 70 Å rms by laser interferometry. Calculated roughnesses based only on the specular reflectivity profiles gave roughnesses of 70 and greater than 90 Å. A layer of Fomblin oil was spun onto the 70 Å rms roughness sapphire sample. Qualitatively, the diffuse scattering is the same as on the uncoated surface; however, quantitative subtle differences are likely and will be examined. 2. Vitreous carbon (VC): two types of VC were polished to measured (by laser interferometry) rms roughness less than 10 Å. STM measurements over >10 areas of the VC-10 give average rms roughness between 14 and 23 Å. Specular analysis of the reflectivity data gives roughness on the same scale. Diffuse scattering has not yet been analyzed. <p>In order to determine the necessary power for laser ablation of the VC surface to provide adequate surface roughening, 5 VC samples were ablated (Tom Jervis) at 0.5, 0.75, 1.0, 1.5 and 2.1 J/cm². STM measurements of the ablated VC gave rms roughnesses of 17-34 Å, 38-53 Å, not measured, 75-95 Å and 31-50 Å respectively. Notice that at 2.1 J/cm², the rms roughness decreases, probably due to local heating and melting of the surface. The granularity of the ablation can be clearly seen in the STM images and will not be presented here. The images will be used to determine height-height correlations for comparison with the reflectivity data.</p> <p>A thin film of Fomblin was spread on the VC surface by dipping in a Freon/Fomblin solution. The diffuse scattering is qualitatively the same as on the uncoated VC as well and quantitative differences will be examined.</p> <ol style="list-style-type: none"> 3. Vanadium/Carbon multilayers (V/CM): 30 bilayers each of 150 Å vanadium and 150 Å carbon were prepared by J. Keem on silicon substrates with a laser interferometry measured rms roughness of 5 Å. Specular and diffuse scattering were taken of these samples. One (V/CM1) sample was laser ablated and measured by reflectometry. The ablated sample was subsequently coated (dipped) with Fomblin and examined by reflectometry. 		

Experiment report (continued):

Comparison to Theory

Recent efforts have been focused on understanding the diffuse scattering from the V/C multilayers using a theory based on the distorted-wave Born approximation [2]. The theoretical results show that if some correlation exists between the layer roughnesses then diffuse scattering is seen in lines of constant q . Presumably, the intensity along one of these q bands is related to the extent of correlation. This work is in progress.

A striking qualitative example of our ability to model the diffuse scattering is shown in Figures 1 and 2. Figure 1 is actual SPEAR data obtained on a V/C multilayer. Figure 2 is the calculated diffuse scattering (specular is not included, thus along $\theta \sim 1$ degree, the experimental data is not represented) using perfect correlation between the layers and about 20 Å rms roughness. We notice that we do indeed have some correlation between the layer roughness in the experimental measurement. Future studies quantitatively analyzing these q bands is continuing.

Figure 1: Plot of total scattering as θ as a function of λ from a 30 bilayer V/C multilayer on silicon. See explanation in text.

References:

- [1] See LANSCE Proposal #5138 and references therein.
- [2] R. Pynn, *Proceedings of SPIE* 1738, 270 (1992) Neutron Optical Devices and Applications

Figure 2: Theoretical plot of theta as a function of lambda (arbitrary scale) for a 30 bilayer V/C multilayer with fully correlated interfacial roughness. Only the diffuse scattering is shown here.

PUB 91 12421

Filter Difference Spectrometer (FDS)

Filter Difference Spectrometer (FDS)

The Filter Difference Spectrometer (FDS) measures changes in the energies of neutrons scattered by a sample in the beam. Scattered neutrons reach the detectors via polycrystalline Be or BeO filters, which will only pass neutrons that fall within the energy bandwidth of the filters. This determines the final energy of the scattered neutrons. Energy transfers can then be calculated from the time of flight of the neutron from the source to the detector. The use of both Be and BeO filters allows different spectra to be taken, which results in much improved resolution. Data can also be corrected using a model filter-response function using either a numerical filter-difference-method or maximum-entropy-method deconvolution. Energy resolution can thereby be improved to a range of 1.5 to 2% of the energy transfer over most of the range of the spectrometer. Because it detects neutrons over a very large solid angle, the FDS is most useful for measurements requiring high sensitivity, such as the vibrations of molecules adsorbed on surfaces.

Instrument Details

Energy-transfer range	100 - 5,000 cm^{-1} (13 - 620 meV)*
Q range	1.5 - 17 $\text{\AA}^{-1}$
Energy-transfer resolution	1.5% - 6.5%, depending on data treatment
Beam size at sample	2.5 cm wide x 10 cm high
Detectors	60 ^3He (1.3 cm diameter)
Filter analyzers	5 Be, 5 BeO, each subtending a scattering angle of 18°; refrigerated
Moderator	Chilled water at 10° C
Sample environment	10 - 300 K, closed cycle refrigerator; furnace temperature limit 400° C
Sample size	0.5 - 100 grams
Experiment duration	2 hours - 2 days

**In certain cases the range can be extended to elastic scattering.*

*Juergen Eckert, instrument scientist
Ross Sanchez, instrument technician*

FDS Experiment reports

5054	<i>Correlation of Proton Dynamics in Manganese Dioxides with Crystalline Structure and Particle Size</i>	182
5130	<i>Determining the Vibrational Modes of Complexed Ammonia in Calcium-Ammonia Intercalate of Titanium Disulfide</i>	184
5160	<i>Hydrogen Bond Dynamics in Quinolinic Acid</i>	186
5168	<i>Models for Biomineralisation Processes</i>	188
5159	<i>The Temperature Dependence of the Vibrational Spectra of Acetanilide and its Isotopomers</i>	190

Experiment report (continued):

types. The higher temperature used in the reduction therefore appears to result in virtually all of the protons being inserted into the channels of the structure.

Shown in Fig. 2 is the spectral difference (Be spectra) between the two MnO_2 samples with grain sizes, respectively, below 30μ and below 80μ . While the differences are indeed small it is nonetheless apparent that the sample with the smaller particle size has excess intensity at about 850 and 1000 cm^{-1} while the larger grain sample may have higher intensity between 600 and 800 cm^{-1} . Both of these samples have a very

Fig. 2 Difference (Be-) spectrum
 $\text{TEKKOSHA MnO}_2 (<80\mu) - \text{MnO}_2 (<30\mu)$.

Fig. 1 INS spectra of TEKKOSHA MnO_2 heated to 450°C for eight days and reduced in cinnamic alcohol at 60°C (top) and 90°C (bottom).

broad band of excitations between 400 and 1100 cm^{-1} which arises¹ from localized protons at various defect sites. The distribution of such sites must therefore differ with grain size.

References:

1. F. Fillaux, H. Ouboumour, J. Tomkinson and L. T. Yu, Chemical Physics 149, 459 (1991).
2. F. Fillaux, H. Ouboumour, C. Cachet, J. Tomkinson, G. J. Kearley and L. T. Yu, (Chem. Phys., in press)

Instrument Used: (please type) FDS	Local Contact Ed Ong	Proposal Number: (for LANSCE Use Only) 5130								
Title: Determining the Vibrational Modes of Complexed Ammonia in Calcium-Ammonia Intercalate of Titanium Disulfide		Report received: (for LANSCE Use Only) 4/5/93								
Authors and affiliations: <table border="0" style="width: 100%;"> <tr> <td style="width: 33%;">E.W. Ong</td> <td>LANSCE, LANL</td> </tr> <tr> <td>J. Eckert</td> <td>LANSCE, LANL</td> </tr> <tr> <td>L.A. Dotson</td> <td>Dept. of Chemistry, Arizona State University</td> </tr> <tr> <td>W.S. Glaunsinger</td> <td>Dept. of Chemistry, Arizona State University</td> </tr> </table>			E.W. Ong	LANSCE, LANL	J. Eckert	LANSCE, LANL	L.A. Dotson	Dept. of Chemistry, Arizona State University	W.S. Glaunsinger	Dept. of Chemistry, Arizona State University
E.W. Ong	LANSCE, LANL									
J. Eckert	LANSCE, LANL									
L.A. Dotson	Dept. of Chemistry, Arizona State University									
W.S. Glaunsinger	Dept. of Chemistry, Arizona State University									
Experiment report: <p>Titanium disulfide, a lamellar chemical compound that has empty spaces between its slabs, has been utilized as the cathode material for high-energy-density lithium batteries. Polar molecules and metals are intercalated between the slabs of titanium disulfide in these applications. The intercalation is accompanied by oxidation of the metal and polar molecules, both as guests between the host slabs. The design of batteries requires detailed understanding about how the various chemical species in them interact on the atomic scale. The rate of charging or recharging for the battery can be limited by how fast the cations can be transported through the electrolyte and the electrodes. The number of charging cycles that a battery can withstand is strongly dependent on the strength of interactions between the cathode material and the guest species that are incorporated. Over wide concentration ranges lithium and the alkaline earth cations form complexes with ammonia within titanium disulfide, with fixed ratios of ammonia-to-cation. The formation of these complexes will effect the transport rate of the cations as well as their interactions with the host.</p> <p>Energy of the vibrations associated with the ammonia species in the intercalates have been studied using the FDS in previous run cycles. Incoherent inelastic neutron spectroscopy was used because of extreme difficulty in obtaining this information by Raman or infrared spectroscopy. During the 1989 run cycle, the vibrational modes of ammonia in the calcium-ammonia intercalates were studied, by varying the calcium concentration. We found that vibrational modes at 245 cm^{-1}, 280 cm^{-1} and 355 cm^{-1} were associated with ammonia not complexed to the calcium ion. Vibrations from ammonia complexed to the calcium cation appeared at energies of 167 cm^{-1} and 470 cm^{-1}. During the 1990 run cycle, these compounds were studied by changing the cations (from calcium to strontium to barium) with the cation concentration kept constant. Confirmation that the 470 cm^{-1} vibration in the calcium intercalates was correctly attributed to the complexed ammonia came from this set of experiment. This high energy vibrational mode systematically shifted to lower energies as the cation "size" is increased. This mode for the Ca^{2+}, Sr^{2+}, and Ba^{2+} compounds has energy at 470 cm^{-1}, 460 cm^{-1}, and 425 cm^{-1}, respectively.</p> <p>During the 1992 run cycle we continued the investigation of calcium-ammonia complexes in titanium disulfide. We investigated the orientational dependence of the molecular vibrations in the intercalates. This was accomplished by probing a sample consisting of fifty calcium-ammonia</p>										

Experiment report (continued):

intercalated TiS_2 crystals mounted on a plate, with the neutron beam oriented parallel and perpendicular to the basal plane of the crystals. The signal intensity of vibrational motions that are parallel to the basal plane increases in the former experiment. Out-of-plane motions will exhibit signals that intensify in the latter experiment. The vibrational motions of the uncomplexed ammonia did not exhibit a strong orientational dependence relative to the host basal plane. It was thought to be held within the host by weak $\text{N-H}\cdots\text{S}$ hydrogen-bonds formed between it and the adjacent host slabs. The $\text{N-H}\cdots\text{S}$ hydrogen-bonds formed between the ammonia molecules and the host slabs are probably so weak that large amplitude librations relative to the basal planes occur. The assignment of the 470 cm^{-1} mode in the calcium-ammonia compounds to the out-of-plane wagging of the complexed ammonia was confirmed by the 1992 experiment. Its signal was more intense when the neutron beam was perpendicular to the host basal plane. The signal of the low energy 167 cm^{-1} showed an opposite trend. It arises from the in-plane rocking of the complexed ammonia. A strong anisotropy for the vibrational energies of the complexed ammonia was expected from the x-ray and neutron diffraction studies, which strongly suggested that the alkaline earth-ammonia complexes are planar. The out-of-plane rocking motion of the complexed ammonia is similar in energy to that associated with the rocking of NH_3 in $[\text{K-NH}_3]^+\text{Cl}^-$ whose value is 460 cm^{-1} . The energy required for the M-NH_3 rocking motions in transition metal $\text{M}(\text{NH}_3)_6$ or $\text{M}(\text{NH}_3)_4$ complexes typically range from 600 cm^{-1} to 900 cm^{-1} . This suggests that the metal-to-ammonia interactions of the intercalated complexes are relatively weak compared to those of transition metal complexes. Preliminary QENS experiments using a calcium-ammonia intercalate has been performed recently at the Intense Neutron Pulse Source (IPNS) at Argonne National Laboratories. The data shows that the complexed ammonia is executing uniaxial rotations parallel to the basal plane of the host.

A more thorough discussion of our findings will be presented in a paper to be published in a future issue of *Chemistry of Materials*.

Due to the scarcity of neutron beam time, this project has taken four years to come to fruition. With the shutting down of the beam lines for LANSCE in 1994, the availability of neutrons for materials science studies is further reduced.

References:

Instrument Used: (please type) FDS	Local Contact Juergen Eckert	Proposal Number: (for LANSCE Use Only) 5160
Title: Hydrogen bond dynamics in quinolinic acid		Report received: (for LANSCE Use Only) 4/29/93
Authors and affiliations: Horst Küppers, Universität Kiel, Germany Juergen Eckert, LANSCE Ed Ong, LANSCE		
Experiment report: As part of our ongoing program to study the dynamics and geometries of extremely short hydrogen bonds ($R(\text{OO}) \sim 2.4 \text{ \AA}$) we have collected the vibrational spectra of single crystals of quinolinic acid (QNA; 2,3-pyridinedicarboxylic acid; $\text{C}_7\text{H}_3\text{H}_2\text{NO}_4$). In a prior experiment ¹ on FDS we obtained data on two polycrystalline samples with the H-bond either protonated or deuterated. Some preliminary assignments of the vibrational modes of the H-bond proton were made on the basis of this H/D substitution experiment. There are two hydrogen bonds in the system ² , a weak $\text{N-H}\cdots\text{O}$ <i>intermolecular</i> H-bond, and a very strong $\text{O}\cdots\text{H}\cdots\text{O}$ <i>intramolecular</i> H-bond (Fig. 1). The latter is highly asymmetric with OH distances of 1.163 and 1.238 $\text{\AA}$. Since the orientation of the molecules in the crystal (space group $P2_1/c$) is such that the H-bond always points in the same direction, additional information on the H-bond vibrations can be obtained by INS studies of single crystals with the H-bond aligned either parallel or perpendicular to Q .		
		Fig. 1 Structure of quinolinic acid determined by neutron diffraction (Ref. 2)

Experiment report (continued):

The spectra obtained on the FDS for three orientations of the crystals at a temperature of approximately 12 K are shown in Fig. 2 in the form of the Maximum Entropy Reconstruction.

In conjunction with our previous data¹ with H/D substitution of the H-bond protons we can tentatively assign the H-bond vibrational modes as follows:

the out-of-plane bending mode $\gamma(\text{OH})$ at 1029 cm^{-1} , the in-plane bending mode $\delta(\text{OH})$ at 1570 cm^{-1} . The asymmetric stretch $\nu_{\text{as}}(\text{OH})$ for this short H-bond may be located at very low frequencies, namely at 596 cm^{-1} .

These assignments are in accord with those expected from correlations^{3,4} of H-bond vibrational frequency vs. geometry. Complete assignments of these spectra are anticipated as a result of normal coordinate analyses currently in progress.

Fig. 2 Oriented single crystal vibrational spectra obtained on FDS. The orientations of Q are (top to bottom): parallel to H-bond; perpendicular in-plane, and perpendicular out-of-plane (of the molecule).

References:

1. H. Küppers and J. Eckert, LANSCE Experiment Reports 1990, LA-12194-PR.
2. F. Takusagawa and T. F. Koetzle, Acta Cryst. B35, 2126 (1979).
3. J. Howard, J. Tomkinson, J. Eckert, J. A. Goldstone and A. D. Taylor, J. Chem. Phys. 78, 3150 (1983).
4. A. Novak, Struct. and Bonding 18, 177 (1974).

Instrument used: (please type) FDS	Local contact: J. ECKERT	Proposal number: (for LANSCE use only) 5168
Title: MODELS FOR BIOMINERALISATION PROCESSES		Report received: (for LANSCE use only) 2/22/93
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div> U.A. JAYASOORIYA A.K. POWELL </div> <div> SCHOOL OF CHEMICAL SCIENCES UNIVERSITY OF EAST ANGLIA NORWICH NR4 7TJ ENGLAND </div> </div>		
Experiment report: <p>We were allocated 3 days beam time on the FDS spectrometer to investigate the OH vibrations in the biomineralisation model compound which has two clusters crystallising in the same lattice. These are the largest synthetic iron clusters known which are likely to be models for the iron storage protein ferritin. Their formulae are $[\text{Fe}_{19}(\mu_3\text{-O})_6(\mu_3\text{-OH})_6(\mu_2\text{-OH})_8(\text{heidi})_{10}(\text{H}_2\text{O})_{12}]^+$ and $[\text{Fe}_{17}(\mu_3\text{-O})_4(\mu_3\text{-OH})_6(\mu_2\text{-OH})_{10}(\text{heidi})_8(\text{H}_2\text{O})_{12}]^{3+}$ where the ligand 'heidi' is given as $\text{H}_3\text{heidi} = \text{N}(\text{CH}_2\text{COOH})_2(\text{CH}_2\text{CH}_2\text{OH})$. The hydroxy hydrogens in these compounds are all inferred and not observed in the x-ray diffraction study. Our original application was to determine the exact structures of these molecules with neutron powder diffraction and then to combine it with the an FDS investigation. However we were unable to obtain beam-time for the earlier experiment, and this has made the analysis of the FDS data difficult. However good spectra of the samples with and without deuteration of the labile protons were obtained, and a difference spectrum is shown in figure 1. The vibrations we expect to see in this spectrum are those due to the water of crystallisation and those due to ligated OH groups. The vibrational frequencies generally expected for water of crystallisation are well documented [1] and easily assigned in this case. The only peaks that are left are a strong broad feature around 1300 to 1400 cm^{-1} containing about three overlapping bands. This then confirms the presense of OH groups and the intensity of these bands suggests a substantial number as assigned in the formula given above. However a more quantitative measurement is only possible with neutron diffraction.</p> <div style="display: flex; align-items: center; justify-content: center;"> <div style="margin-right: 20px;">Figure 1</div> </div>		

Experiment report (continued):

We were also able to study a few more compounds due to the generosity of our local contact. These included obtaining good spectra of α and β glucose and the simplest organic sulphate, potassium methyl sulphate. We are interested in the latter compound as a model for the industrially important complex sulphated polysaccharides like carrageenans. Here we report the preliminary results of the analysis of the FDS spectrum using the CLIMAX program. We have also used a complete set of infrared and Raman spectroscopic data for this analysis and the fit with only the fundamental modes is given in Figure 2a. Here we have used only the principal force constants plus one interaction. Clearly, most of the INS intensity is due to the overtones, combinations and phonon wings. A fit with all these included are shown in Figure 2b. An interesting outcome of this study is the assignment of the torsional mode of the SO_3 group. This mode is neither infrared nor Raman active and at first was not expected to show any INS intensity because of the very low scattering cross-sections of the atoms involved. However we found that it was impossible to get any semblance of a fit without the inclusion of this mode whose coupling to the CH_3 torsion is clearly of importance in the understanding of the INS spectrum. The reported fit to the INS spectrum gives us a value of 46 cm^{-1} for the SO_3 torsion. This to the best of our knowledge is the first ever assignment of such a mode.

Figure 2

References:

- 1 H.D. Lutz, *Structure and Bonding*, **69** (1988) 98.

Instrument Used: <i>(please type)</i> FDS	Local Contact Juergen Eckert	Proposal Number: <i>(for LANSCE Use Only)</i> 5159
Title: The Temperature Dependence of the Vibrational Spectra of Acetanilide and its Isotopomers		Report received: <i>(for LANSCE Use Only)</i> 4/12/93
Authors and affiliations: Mariette Barthes, Universite des Sciences, Montpellier (France) Juergen Eckert, LANSCE Susanna W. Johnson, LANSCE		
Experiment report: <div style="text-align: right;"><i>J. Phys. I France</i> 2 (1992) 1929-1939</div> <div style="text-align: right;">OCTOBER 1992, PAGE 1929</div> <div> Classification <i>Physics Abstracts</i> 34.30 — 34.50 </div> <div style="text-align: center;"> Anomalous vibrational modes in acetanilide as studied by inelastic neutron scattering </div> <div> Mariette Barthes ⁽¹⁾, Juergen Eckert ⁽²⁾, Susanna W. Johnson ⁽²⁾, Jacques Moret ⁽¹⁾, Basil I. Swanson ⁽³⁾ and Clifford J. Unkefer ⁽³⁾ </div> <div> ⁽¹⁾ Groupe de Dynamique des Phases Condensées, Université des Sciences, 34095 Montpellier, France ⁽²⁾ LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A. ⁽³⁾ INC4, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A. </div> <div> Abstract. — A study of the anomalous modes in acetanilide and five deuterated derivatives by incoherent inelastic neutron scattering is reported. These data show that the dynamics of the amide and methyl groups influence each other. In addition, the anomalous temperature behaviour of the NH out-of-plane bending mode is confirmed. These observations suggest that the self-trapping mechanism in ACN may be more complex than hitherto assumed. </div>

CN 93 437

PHAROS

Chopper Spectrometer (PHAROS)

The new chopper spectrometer, PHAROS, is intended to provide 0.5% incident energy resolution for incident energies between 50 meV and 2 eV. The spectrometer is located on flight path 16 with a sample position 20 m from the moderator, which is currently water at room temperature.

Phase I of the construction is ready (Fig. a) and consists of an evacuated, shielded flight path for low-angle scattering ($1^\circ < \theta < 12^\circ$). The spectrometer is suitable for low-angle studies such as neutron Brillouin scattering and magnetic excitations.

When Phase II of the construction is completed (Fig. b), the spectrometer will be a high-resolution, general-purpose chopper spectrometer with 10 m^2 of detectors covering scattering angles between -10° and 140° . PHAROS will then be able to accommodate the full range of inelastic scattering experiments, including phonon density of states, magnetic excitations, momentum distributions, crystal-field levels, chemical spectroscopy, and measurements of $S(Q, \omega)$ in disordered systems. In addition, it will be possible to use the low-angle detectors at distances between 4 and 10 m, with scattering angles down to 1° , and will be suitable for high-resolution inelastic studies at low Q .

Instrument Details

Moderator-chopper distance	18 m
Chopper-sample distance	2 m
Moderator	12.5 x 12.5 cm ² room temperature H ₂ O
Chopper frequency	600 Hz
Chopper diameter	10 cm
Chopper slit spacing	1 mm or more
Sample size	up to 5 cm x 7.5 cm
Incident energy resolution	$\Delta E_i/E_i = 0.5\%$

Phase I

1 m² of detectors at 3.5 m from the sample; scattering angle between 1° and 12°.

Phase II (1993)

9 m² of detectors at 4 m from the sample; scattering angle between -10° and 140°;

1 m² of detectors in forward scattering position at 4 - 10 m from the sample

Robert Robinson, instrument scientist

Eric Larson, instrument technician

LANSCE file photo

Appendices

1 9 9 1
 DISTINGUISHED
 PERFORMANCE
 AWARDS

The Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) is a national user facility for neutron scattering experiments that is used by scientists worldwide. When, after five years of successful operation, the liquid hydrogen moderator began to leak, this multidisciplinary and multidivisional team of volunteers came together to repair and replace the moderator in the LANSCE target assembly. The repair

was carried out against the clock of arriving outside users and within the challenges and constraints presented by the Tiger Team requirements. Completion of the task involved long, uncomfortable hours of work and an extraordinary level of teamwork. The work was accomplished within a week of the scheduled deadline. Completing the repair project brought distinction to the Laboratory within the DOE and with LANSCE users from around the world.

-
- James Abernathy, MP-7
 Elizabeth Ares, HS-1
 Guy Baker, LANSCE
 Mark Bayless, HS-1
 Robert Beistel, HS-1
 Michael Borden, MP-5
 Roland Brewton, LANSCE
 Art Bridge, LANSCE
 Torben Brun, LANSCE
 Glenn Camp, MP-7
 Stanley Chance, MP-5
 Sonny Cordova, MP-8
 Robert Damjanovich, MP-5
 Dan Davis, LANSCE
 Maria DiStravolo, LANSCE
 David Dorsey, HS-1
 Deirdre Espinoza, LANSCE
 Phillip Ferguson, MP-5
 Gail Flower, IS-1
 Kandy Frame, MP-5
 Julian Garcia, MP-7
 Al Gjovig, LANSCE
 Joyce Goldstone, LANSCE
 Blaine Hadden, LANSCE
 Rod Hardee, LANSCE
 Ray Harris, HS-1
 William Haynes, HS-1
 Rex Hjelm, LANSCE
 David Honabarger, MP-4
 Thomas Houle, HS-1
 Harry Howard, LANSCE
 John Jameson, HS-1
 Jack Johnson, HS-1
 Alan Kernodle, LANSCE
 Douglas Knutt, MP-7
 James Larkin, HS-1
 Eric Larson, LANSCE
 James Ledbetter, MST-5
 Manuel Lopez, MST-5
 Kathy Lovell, LANSCE
 Alfred Maestas, MP-5
 Robert Mansfield, HS-1
 Dennis Martinez, LANSCE
 Johnny Martinez, HS-1
 Patrick McClellan, MP-8
 Gilbert Merriman, HS-1
 Donald Mikkelson, HS-1
 Ron Nelson, LANSCE
 Felix Olivas, MP-5
 Bert Ortiz, MP-5
 Michael Peraglio, MP-5
 Michael Perez, MP-8
 Roger Pynn, LANSCE
 John Quicksilver, LANSCE
 Harold Robinson, LANSCE
 Rob Robinson, LANSCE
 Frank Romero, MP-8
 Tobias Romero, MST-5
 Gary Russell, LANSCE
 Richard Ryder, MP-5
 Jesse Salazar, HS-1
 Ross Sanchez, LANSCE
 John Sandoval, LANSCE
 John Seal, LANSCE
 Phil Seeger, LANSCE
 Greg Smith, LANSCE
 Walter Sommer, MP-5
 Connie Stephens, HS-1
 Robert Stokes, HS-1
 Kit Taylor, MP-5
 John Thomas, LANSCE
 Bob VonDreele, LANSCE
 Scott Walker, HS-1
 Joseph Weber, HS-1
 Edward Weiler, MP-8

Publication list

Condensed Matter Research Published Articles

D. L. Bish and C. W. Burnham, "Rietveld Refinement of the Crystal Structure of Fibrolitic Sillimanite Using Neutron Powder Diffraction Data," *American Mineralogist* **77**, 374-379 (1992).

S. L. Blechner, G. A. Olah, N. Strynadka, C.-L. A. Wang, H. B. Struhmann, and J. Trehwella, "Small-Angle Solution Scattering Studies of TnC Dimers and Monomers, Their Interactions with Peptides and with TnI," *Biophysical Journal* **61**, A470 (1992).

A. Bulou, S. Hockett, E. Garcia, B. I. Swanson, G. H Kwei, and J. Eckert, "Structural Phase Transition in Quasi-One-Dimensional PtCl," *Ferroelectrics* **125**, 45-50 (1992).

E. Burkel, **M. R. Fitzsimmons**, and M. Müller-Stach, "Reflectivity Studies of Thin Au Films and Au Bicrystals with Grain Boundaries," *Springer Proceedings in Physics* **61**, 181-185 (1992).

J. A. Eastman, **M. R. Fitzsimmons**, M. Müller-Stach, G. Wallner, and W. T. Elam, "Characterization of Nanocrystalline PD by X-ray Diffraction and EXAFS," *Nanostructured Materials* **1**, 47 (1992).

J. Eckert, A. Albinati, R. P. White, C. Bianchini, and M. Peruzzini, "The Barrier to Rotation of the Dihydrogen Ligand in the Complexes [MH(p2-H2)PP3]BPh4, M=Fe, Ru: Evidence for Stronger Backdonation in the Fe-Complex," *Inorganic Chemistry* **31** (21), 4241-4244 (1992).

J. B. Field, C. Toprakcioglu, R. C. Ball, H. B. Stanley, L. Dai, W. Barford, J. Pendfold, **G. S. Smith**, and W. Hamilton, "Determination of End-Absorbed Polymer Density Profiles by Neutron Reflectometry," *Macromolecules* **25**, 434-439 (1992).

J. B. Field, C. Toprakcioglu, L. Dai, G. Hadziioannou, **G. S. Smith**, and W. A. Hamilton, "Neutron Reflectivity Study of End-Adsorbed Diblock Copolymers: Cross-Over From Mushrooms to Brushes," *Journal de Physique II France* **2**, 2221-2235 (1992).

S. J. Henderson, P. Newsholme, D. B. Heidorn, R. Mitchell, **P. A. Seeger**, D. A. Walsh, and J. Trehwella, "The Solution Structure of Phosphorylase Kinase Studied Using Small-Angle X-ray and Neutron Scattering," *Biochemistry* **31** (2), 437-442 (1992).

J. Hriljac, J. B. Parise, G. H. Kwei, and K. B. Schwartz, "The Synthesis and ab initio Crystal Structure Determination of Cu Pt3O6 From a Combination of Powder X-ray and Neutron Data," *Journal of Physics and Chemistry of Solids* **52**, 1273 (1991).

Publications

- H. Hwang, S.-W. Cheong, A. S. Cooper, L. W. Rupp, Jr., B. Batlogg, G. H. Kwei, and Z. Tan, "Crystallographic Evolution, $T^* > T > T_c$, in $\text{Pr}_{2-x}\text{Sr}_x\text{CuO}_{4-d}$," *Physica C* **192**, 362 (1992).
- L. Jong, T. K. Kwei, E. Pearce, **G. S. Smith**, W. Hamilton, and G. H. Kwei, "Neutron Reflectivity Studies of Phase Separation of Polymer Blends," *Macromolecules* **25**, 6670 (1992).
- L. Jong, E. M. Pearce, T. K. Kwei, W. A. Hamilton, **G. S. Smith**, and G. H. Kwei, "Neutron Reflectivity Study of Thin Films of Hydrogen-Bonded Polymer Blends: Influence of Annealing on Composition Profile," *Macromolecules* **25**, 2619-2623 (1992).
- K. A. Kubat-Martin, G. H. Kwei, A. C. Lawson, and D. E. Peterson, "Structure, Cation Ordering and Oxygen Stoichiometry in $\text{CaBa}_4\text{Cu}_3\text{O}_{8+d}$," *Journal of Solid State Chemistry* **100**, 130 (1992).
- G. H. Kwei, J. M. Lawrence, W. P. Beyerman, P. C. Canfield, J. D. Thompson, Z. Fisk, A. C. Lawson, and **J. A. Goldstone**, "Thermal Expansion of $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ at Ambient and High Pressure," *Physics Review, B* **46** (13), 8067-8072 (1992).
- G. H. Kwei, K. C. Ott, and E. J. Peterson, "Neutron Powder Diffraction Study of Cu-Site Preference of Li Dopants in $\text{YBa}_2(\text{Cu}_{1-x}\text{Li}_x)_3\text{O}_{6+d}$," *Physica C* **194**, 307-320 (1992).
- A. Larceda, P. C. Canfield, W. P. Beyermann, M. F. Hundley, J. D. Thompson, G. Sparn, Z. Fisk, C. Burns, D. Barnhart, A. C. Lawson, G. H. Kwei, and **J. A. Goldstone**, "Possible Heavy-Fermion Behaviour and Field-Induced Transition in New R-Pt-Ga Compounds," *Journal of Alloys and Compounds* **181**, 191-196 (1992).
- H. Maletta, **R. A. Robinson**, A. C. Lawson, V. Sechovsky, L. Havela, L. Jirman, M. Divis, E. Bruck, F. R. de Boer, A. V. Andreev, and K. H. Buschow, "On the Magnetic Structure of UNiGa ," *Journal of Magnetism and Magnetic Materials* **104**, 21-22 (1992).
- J. T. Mang, T. P. Rieker, L. Chen, P. Patel, V. Surendranath, and S. Kumar, "Critical Behavior at the Nematic to Smectic-A Phase Transition in a Side Chain Polymer Liquid Crystal," *Polymer Science and Materials Engineering* **67**, P376 (1992).
- B. Morosin, G. H. Kwei, J. E. Schirber, J. A. Voigt, E. L. Venturini, and **J. A. Goldstone**, "Superconducting Superoxygenated $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+d}$: Search for Phase Separation," *Physica C* **185**, 565-566 (1991).
- J. B. Parise, R. E. Harlow, R. D. Shannon, G. H. Kwei, T. H. Allik, and J. T. Armstrong, "Crystal Structure and Electron Microprobe Analyses of a Lanthanum Lutetium Gallium Garnet," *Journal of Applied Physics* **72** (6), 2152-2155 (1992).
- I. J. Pickering, J. T. Lewandowski, A. J. Jacobson, and **J. A. Goldstone**, "A Neutron Powder Diffraction Study of the Ordering of $\text{Li}_x\text{Ni}_{1-x}\text{O}$," *Solid State Ionics* **53-6**, 405-412 (1992).
- G. L. Povirk, M. G. Stout, **M. A. Bourke**, **J. A. Goldstone**, A. C. Lawson, M. Lovato, S. R. MacEwen, S. R. Nutt, and A. Needleman, "Thermally and Mechanically Induced Residual Strains in Al-SiC Composites," *Acta Metallurgica* **40**, 2391-2412 (1992).
- R. Pynn**, "Neutron Scattering by Rough Surfaces at Grazing Incidence," *Physical Review, B* **45**, 602-612 (1992).
- R. A. Robinson**, A. C. Lawson, J. W. Lynn, and K. H. Buschow, "Temperature Dependence of Magnetic Order in UPdSn ," *Physical Review, B* **45** (6), 2939-2944 (1992).
- T. R. Sosnick, D. C. Benjamin, J. Novotny, **P. A. Seeger**, and J. Trehwella, "Distances Between the Antigen Binding Sites of Three Murine Antibody Subclasses Measured Using Neutron Scattering and X-ray Scattering," *Biochemistry* **31** (6), 1779-1786 (1992).

T. Sosnick, S. Charles, G. Stubbs, P. Yau, E. M. Bradbury, P. Timmins, and J. Trehwella, "Orienting Rigid and Flexible Biological Assemblies in Ferrofluids for Small-Angle Neutron Scattering Studies," *Biophysical Journal*, 1178-1189 (1991).

J.-B. Suck, P. A. Egelstaff, **R. A. Robinson**, D. S. Sivia, and A. D. Taylor, "Brillouin Scattering with Neutron in an Amorphous Solid," *Europhysics Letters* **19** (3), 207-213 (1992).

J. Trehwella, "The Solution Structures of Calmodulin and its Complexes with Peptides Based on Target Enzyme Binding Domains," *Cell Calcium* **13** (6-7), 377-390 (1992).

J. W. Ward, B. Cort, **J. A. Goldstone**, A. C. Lawson, L. E. Cox, and R. G. Haire, "Electronic, Structural, and Transport Properties of (Almost) Rare-Earth-Like Actinide Hydrides," *Journal of the American Chemical Society* **114**, 404-415 (1992).

J. K. Warner, A. K. Cheetham, D. E. Cox, and **R. B. Von Dreele**, "Valence Contrast between Iron Sites in α -Fe₂PO₅: A Comparative Study by Magnetic Neutron and Resonant X-ray Powder Diffraction," *Journal of the American Chemical Society* **114**, 6074-6080 (1992).

Publications in Press or Submitted

A. Albinati, **J. Eckert**, P. Hofmann, H. Ruediger, and L. M. Venanzi, "Theoretical and Spectroscopic Studies of Tetrahedral Clusters of the type $[L_3M(m-H)_x(AuL')_3]^{2+}$ (M = Rh and Ir, x = 2; M = Ru, x = 3)," Los Alamos National Laboratory document LA-UR-92-2638 (submitted to *Journal of the American Chemical Society*).

M. A. Bourke, **J. A. Goldstone**, M. G. Stout, and A. Needleman, "Characterization of Residual Stresses in Composites," Los Alamos National Laboratory document LA-UR-92-2479 (to be published in *Fundamentals of Metal-Matrix Composites*, S. Suresh, A. Mortensen, and A. Needleman, Eds., Butterworth-Heinemann, Stoneham, Massachusetts).

J. A. Eastman, **M. R. Fitzsimmons**, and L. J. Thompson, "The Thermal Properties of Nanocrystalline Pd from 16-300K," Los Alamos National Laboratory document LA-UR-92-1310 (to be published in *Philosophical Magazine*, B).

M. R. Fitzsimmons and E. Burkel, "Interfacial Roughness of [001] Twist Grain Boundaries Characterized with X-ray Reflectivity," Los Alamos National Laboratory document LA-UR-92-3253 (submitted to *Physical Review*, B).

M. J. Geselbracht, A. M. Stacy, A. R. Garcia, B. G. Silbernagel, and G. H. Kwei, "Local Environment and Lithium Ion Mobility in LiNbO₂: Inferences from Structure, Physical Properties, and NMR" (submitted to *Journal of Physical Chemistry*).

R. P. Hjelm, P. Thiyagarajan, and M. H. Alkan, "The Organization of Phosphatidylcholine and Bile Salt in Rod-Like Mixed Micelles," Los Alamos National Laboratory document LA-UR-92-1715 (to be published in *Journal of Physical Chemistry*).

R. P. Hjelm, W. A. Wampler, and **P. A. Seeger**, "Microstructure of Composite Materials Using Small-Angle Neutron Scattering and Contrast Variation: Approaches Toward Understanding the Structure of Carbon Black-Elastomer Mixtures," Los Alamos National Laboratory document LA-UR-92-3273 (submitted to *Composite Polymers*).

R. P. Hjelm, J. Wilcoxon, P. Thiyagarajan, and H. Alkan, "Non-Equilibrium Behaviour in Egg Phosphatidylcholine-Bile Salt Mixed Aqueous Colloids," Los Alamos National Laboratory document LA-UR-92-3272 (submitted to *Croatica Chemica Acta*).

S. W. Johnson, M. F. Nicol, and D. Schiferl, "Algorithm for Sorting Diffraction Data From a Sample Consisting of Several Crystals Enclosed in a Sample Environment Apparatus," Los Alamos National Laboratory document LA-UR-92-767 (submitted to *Journal of Applied Crystallography*).

S. W. Keller, V. A. Carlson, A. M. Stacy, G. H. Kwei, and M. Alario-Franco, "A New Series of Magnetic Rare Earth Cuprates: RCu_2O_4 ($\text{R} = \text{La}, \text{Nd}, \text{Sm}, \text{and Eu}$)," Los Alamos National Laboratory document LA-UR 91-3761 (submitted to *Nature*).

G. J. Kubas, C. J. Burns, J. Eckert, S. W. Johnson, A. C. Larson, P. J. Vergamini, C. J. Unkefer, G. R. K. Khalsa, S. A. Jackson, and O. Eisenstein, "Neutron Structure and Inelastic Neutron Scattering and Theoretical Studies of Molybdenum (Carbonyl) (Dihydrogen) BIS (Diphenylphosphinoethane), (4.5 Benzene), A Complex with an Extremely Low Barrier to Dihydrogen Rotation. Implications on the Reaction Coordinate for H-H Cleavage to Dihydride," Los Alamos National Laboratory document LA-UR-92-1502 (submitted to *Journal of the American Chemical Society*).

G. H. Kwei, S. J. Billinge, A. C. Larson, and S.-W. Cheong, "Structure and Phase Transitions in Three Low Temperature Phases of Barium Titanate," (submitted to *Journal of Physical Chemistry*).

G. H. Kwei, J. O. Willis, J. A. Goldstone, A. C. Lawson, T. Sakurai, H. Yamauchi, and S. Tanaka, "Dopant Solubility, Phase Stability, and Superconductivity in Sr-Doped $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$," Los Alamos National Laboratory document LA-UR-92-2234 (submitted to *Physica C*).

H. B. Liu, D. E. Morris, A. P. Sinha, and G. H. Kwei, "Effect of Praseodymium Substitution in $\text{YBa}_2\text{Cu}_4\text{O}_8(1:2:4)$ " (to be published in *Physica C*).

L. Liu and T. O. Brun, "Anisotropic Vortex-Flux Rotation in Grain-Oriented $\text{YBa}_2\text{Cu}_3\text{O}_7$," Los Alamos National Laboratory document LA-UR-92-1033 (submitted to *Physical Review*).

H. Nakotte, R. A. Robinson, J. W. Lynn, E. Brück, and F. R. de Boer, "Field-Induced Transition in UPdSn at 3T," Los Alamos National Laboratory document LA-UR-92-1856 (to be published in *Physical Review, B*).

D. E. Partin, G. H. Kwei, and M. O'Keefe, "Neutron Powder Diffraction Studies of the Structures of SrCuO_2 and Sr_2CuO_3 ," (submitted to *Journal of Solid State Chemistry*).

T. P. Rieker, C. Haltiwanger, K. Eidman, D. W. Walba, N. A. Clark, and A. C. Larson, "The Crystal Structure of 2-Phenylacetophenone," Los Alamos National Laboratory document LA-UR-92-3246 (to be published in *Acta Crystallographica, Section C*).

R. A. Robinson, J. W. Lynn, V. Nunez, K. H. Buschow, H. Nakotte, and A. C. Lawson, "Crystallographic and Magnetic Properties of UAuSn ," Los Alamos National Laboratory document LA-UR-92-2375 (to be published in *Physical Review, B*).

R. A. Robinson, A. C. Lawson, J. W. Lynn, and K. H. Buschow, "Incommensurate Magnetic Order in UPtGe ," Los Alamos National Laboratory document LA-UR-92-87 (to be published in *Physical Review, B*).

J. D. Thompson, W. P. Beyermann, P. C. Canfield, M. F. Hundley, G. H. Kwei, A. Lacerda, Z. Fisk, R. S. Kowk, J. M. Lawrence, and A. Severing, "Thermodynamics and Transport in $\text{Ce}_3\text{Bi}_4\text{Pt}_3$ and Related Materials," Los Alamos National Laboratory document LA-UR 92-2800 (to be published in *Transport and Thermal Properties of Electron Systems*, H. Fujii, T. Fujita, and G. Oomi, Eds., Plenum Press, New York, 1993).

B. H. Torrie, R. B. Von Dreele, and A. C. Larson, "Structure of Solid Cyanamide at 13K," Los Alamos National Laboratory document LA-UR-92-3216 (submitted to *Journal of Molecular Physics*).

J. Zhang, R. B. Von Dreele, and L. Eyring, "The Structures of Tb_7O_{12} and $\text{Tb}_{11}\text{O}_{20}$," Los Alamos National Laboratory document LA-UR-92-2283 (to be published in *Journal of Solid State Chemistry*).

Contributed Conference Presentations

M. A. Bourke, J. A. Goldstone, and F. Guerra, "Stress Redistribution in Cracked Autofrettaged Tubing," Forty-first Annual Conference on Applications of X-ray Analysis, Colorado Springs, Colorado, August 3-7, 1992, Los Alamos National Laboratory document LA-UR-92-1492.

M. A. Bourke, J. A. Goldstone, M. G. Stout, A. C. Lawson, and J. E. Allison, "Strain Measurement in Individual Phases of an Al/TiC Composite During Mechanical Loading," 122nd TMS Annual Meeting, Denver, Colorado, February 21-25, 1993, Los Alamos National Laboratory document LA-UR-92-1430.

M. A. Bourke, J. A. Goldstone, M. G. Stout, and A. C. Lawson, "Strain Measurement in Individual Phases of Composites During Thermo-Mechanical Loading," 122nd TMS Annual Meeting, Denver, Colorado, February 21-25, 1993, Los Alamos National Laboratory document LA-UR-92-1430.

J. A. Eastman, **M. R. Fitzsimmons,** and L. J. Thompson, "X-ray Diffraction Studies of the Thermal Properties of Nanophase Pd and TiO₂," First International Conference on Nanostructured Materials, Cancun, Mexico, September 22-26, 1992, Los Alamos National Laboratory document, LA-UR-92-1308.

M. R. Fitzsimmons, J. A. Eastman, **R. A. Robinson,** A. C. Lawson, G. H. Kwei, K. E. Sickafus, M. A. Nastasi, and E. Burke, "Magnetic Structures of Nanometer Scale Dy, Cr, and Ni," First International Conference on Nanostructured Materials, Cancun Mexico, September 21-25, 1992, Los Alamos National Laboratory document LA-UR-92-3385.

M. R. Fitzsimmons, J. A. Eastman, **R. A. Robinson,** K. E. Sickafus, M. R. Mueller-Stach, and E. Burke, "The Atomic and Magnetic Structures of Nanophase-Dy and Cr and Twist Grain Boundaries in Ni," First International Conference on Nanostructured Materials, Cancun, Mexico, September 22-26, 1992, Los Alamos National document LA-UR-92-1428.

G. T. Gray III, C. E. Morris, and A. C. Lawson, "Omega Phase Formation in Titanium and Titanium Alloys," Seventh World Conference on Titanium, The Minerals, Metals and Materials Society (TMS), San Diego, California, June 28-July 2, 1992, Los Alamos National Laboratory document LA-UR-92-0087.

M. R. James, **M. A. Bourke, J. A. Goldstone,** and A. C. Lawson, "Diffraction Measurements of Residual Stress in Titanium Matrix Composites," 122nd TMS Annual Meeting, Denver, Colorado, February 21-25, 1993, Los Alamos National Laboratory document LA-UR 92-3831.

M. R. James, **M. A. Bourke, J. A. Goldstone,** and A. C. Lawson, "Residual Stress Measurements in Continuous Fiber Titanium Matrix Composites," Forty-first Annual Conference on Applications of X-ray Analysis, Colorado Springs, Colorado, August 3-7, 1992, Los Alamos National Laboratory document LA-UR-92-3368.

S. W. Johnson, J. Eckert, and J. D. Thompson, "Investigation of the Vibrational Coupling in Organic Molecular Crystals at High Pressure Using Inelastic Neutron Scattering," European Workshop on Neutron Scattering at High Pressures, Abingdon, Oxfordshire, United Kingdom, March 18-21, 1992, Los Alamos National Laboratory document LA-UR-92-873.

S. W. Johnson, A. C. Larson, and **J. Eckert,** "The Neutron Structure of Acetanilide at Low Temperature: Indirect Evidence For the Existence of Non-Linear Excitations," The 1992 Annual Meeting of the American Crystallographic Association, Pittsburgh, Pennsylvania, August 9-14, 1992, Los Alamos National Laboratory document LA-UR-92-1307.

S. W. Johnson, R. A. Robinson, H. Nakotte, E. Brück, F. R. de Boer, and **A. C. Larson,** "Crystallographic and Magnetic Properties of UAuSn," Magnetism and Magnetic Materials Conference, Houston, Texas, December 1-4, 1992, Los Alamos National Laboratory document LA-UR-92-2375.

T. Johnston, D. L. Bish, J. Eckert, and L. A. Dotson, "Molecular Probe Studies of the Kaolinite Surface Using Hydrazine," Twenty-ninth Annual Meeting of the Clay & Minerals Society, Minneapolis, Minnesota, November 1-6, 1992, Los Alamos National Laboratory document LA-UR-92-2937.

A. C. Larson and R. B. Von Dreele, "GSAS Progress Report for 1992, Magnetic Structures and UNIX," The 1992 Annual Meeting of the American Crystallographic Association, Pittsburgh, Pennsylvania, August 9-14, 1992, Los Alamos National Laboratory document LA-UR-92-1270.

A. C. Lawson, G. H. Kwei, J. A. Goldstone, B. Cort, D. Eash, R. J. Martinez, R. Sheldon, and L. Foltyn, "Measurement of Atomic Elastic Constants by Pulsed Neutron Diffraction," Forty-first Annual Conference on Applications of X-ray Analysis, Colorado Springs, Colorado, August 3-7, 1992, Los Alamos National Laboratory document LA-UR-92-1119.

J. T. Mang, P. Pater, S. T. Shin, S. Kumar, and T. P. Rieker, "Nematic to Smectic-A Phase Transition in a Side Chain Liquid Crystal Polymer: A SANS and High-Resolution X-ray Scattering Study," The 14th International Liquid Crystal Conference, Pisa, Italy, June 21-26, 1992, Los Alamos National Laboratory document LA-UR-92-3295.

J. T. Mang, P. Patel, S. T. Shin, S. Kumar, and T. P. Rieker, "SANS and X-ray Scattering Study of the Nematic to Smectic-A Phase Transition in a Side Chain Polymer," The 101st Meeting of the Ohio Academy of Science, Akron, Ohio, May 1, 1992, Los Alamos National Laboratory document LA-UR-92-3296.

J. T. Mang, P. Patel, V. Surendranath, S. Kumar, and T. P. Rieker, "Radius of Gyration in the Smectic-A and Nematic Phases of a Side-Chain Polymer Liquid Crystal," American Physical Society Spring Meeting, Indianapolis, Indiana, March 16-20, 1992, Los Alamos National Laboratory document LA-UR-92-3251.

H. Nakotte, E. Brück, F. R. de Boer, P. Svoboda, N. C. Tuan, L. Havela, V. Sechovsky, and R. A. Robinson, "Antiferromagnetic Domains in UPdSn," Magnetism and Magnetic Materials Conference, Houston, Texas, December 1-4, 1992, Los Alamos National Laboratory document LA-UR-92-2695.

J. E. Nelson, J. Eckert, and G. J. Kubas, "Synthesis, Characterization, and Spectroscopic Investigations of $\text{Cr}(\text{CO})_3(\text{PCy}_3)_2(\text{h}^2\text{-H}_2)$," American Chemical Society Technical Symposium, San Francisco, California, April 5-10, 1992, Los Alamos National Laboratory document LA-UR-92-3721.

T. P. Rieker and N. A. Clark, "The Layer and Director Structures of Ferroelectric Liquid Crystals," in *Phase Transitions in Liquid Crystals*, S. Martelluci and A. N. Chester, Eds. (Plenum Press, Sicily, Italy, 1991), Vol. 290, pp. 287-341.

T. P. Rieker, E. Janulis, and C. Safinya, "X-ray Investigation of Surface Induced Molecular Ordering in the Smectic A and C Phases of Highly Fluorinated Thermotropic Liquid Crystals," The 14th International Liquid Crystal Conference, Pisa, Italy, June 21-26, 1992, Los Alamos National Laboratory document LA-UR-92-600.

T. P. Rieker, R. B. Von Dreele, and R. P. Hjelm, "Neutron Powder Diffraction Investigation of the Nematic, Smectic A, and Smectic C Phases of a Highly Deuterated Thermotropic Liquid Crystal," The 14th International Liquid Crystal Conference, Pisa, Italy, June 21-26, 1992, Los Alamos National Laboratory document LA-UR-92-599.

R. A. Robinson, M. Kohgi, T. Osakabe, P. C. Canfield, T. Kamiyama, T. Nakane, and Z. Fisk, "Crystal Field Levels In YbBiPt," The International Conference on Strongly Correlated Electron Systems, Sendai, Japan, September 7-11, 1992, Los Alamos National Laboratory document LA-UR-92-2578.

H. Senapati, R. P. Hjelm, P. A. Seeger, T. P. Rieker, and C. A. Angell, "Small Angle Neutron Scattering Studies of Droplet Equilibrium in Oil-in-Water Microemulsions," American Physical Society Spring Meeting, Indianapolis, Indiana, March 16-20, 1992, Los Alamos National Laboratory document LA-UR-92-3997.

G. S. Smith, W. Hamilton, **M. Fitzsimmons**, **S. M. Baker**, K. M. Hubbard, M. Nastasi, J.-P., Hirvonen, and T. G. Zocco "Neutron Reflectometry Study of Thermally Induced Boron Diffusion in Amorphous Elemental Boron," in *Neutron Optical Devices and Applications*, C. F. Majkrzak and J. L. Wood, Eds. (The Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1992) Proc. SPIE Vol. 1738, pp. 246-253.

S. Spooner, S. A. David, J. H. Root, T. M. Holden, **M. A. Bourke**, and **J. A. Goldstone**, "Residual Stress and Strain Measurement in an Austenitic Steel Plate Containing a Multipass Weld," Third International Conference on Trends in Welding Research, Gatlinburg, Tennessee, June 1-5, 1992, Los Alamos National Laboratory document LA-UR-92-1528.

J. Trehwella, "Neutron and X-ray Scattering Studies of the Interactions Between Ca^{2+} - Binding Proteins and their Regulatory Targets: Comparisons of Troponin C and Calmodulin," The 4th International Conference on Biophysics and Synchrotron Radiation, Tsukuba, Japan, August 30-September 5, 1992, Los Alamos National Laboratory document LA-UR-92-1590.

T. G. Zocco, A. C. Lawson, **P. A. Seeger**, J. R. Cost, and R. J. Martinez, "Aging Studies of a PU-GA Alloy by Small Angle Neutron Scattering (SANS)," JOWOG 22A, Aldermaston, United Kingdom, October 5, 1992, Los Alamos National Laboratory document LA-UR-92-0311.

Invited Talks

A. Albinati and **J. Eckert**, "Structure and Dynamics of the "H₂" Ligand in Transition Metal Complexes," Riunione degli Utilizzatori della Spettroscopia Neutronica, Rome, Italy, February 17-18, 1992, Los Alamos National Laboratory document LA-UR-92-1235.

M. Barthes, H. Kellouai, G. Page, J. Moret, **J. Eckert**, and **S. W. Johnson**, "New Self-Trapped Amides Modes in Chains of Hydrogen-Bonded Molecules," NATO Workshop on Future Directions in Non-Linear Dynamics, Copenhagen, Denmark, July 22-30, 1992, Los Alamos National Laboratory document LA-UR-92-2156.

M. Barthes, H. Kellouai, G. Page, J. Moret, **S. W. Johnson**, and **J. Eckert**, "H-Localized Mode in Chains of Hydrogen-Bonded Amide Group," Future Direction in Nonlinear Dynamics, Copenhagen, Denmark, July 22-30, 1992, Los Alamos National Laboratory document LA-UR-92-3333.

J. A. Eastman, **M. R. Fitzsimmons**, A. C. Lawson, **R. A. Robinson**, L. J. Thompson, and J. Satti, "Information on Grain Boundary Structure in Nanocrystalline Pd and Cr from Diffraction Studies," The 6th International Conference of Intergranular and Interphase Boundaries in Materials (iib92), Thessalonik, Greece, June 21-26, 1992, Los Alamos National Laboratory document LA-UR-92-3369.

R. P. Hjelm and **P. A. Seeger**, "Solutions for Implementing Time-of-Flight Techniques in Low-Angle Neutron Scattering, As Realized on the Low-Q Diffractometer at Los Alamos," International Seminar on Structural Investigation in Pulsed Sources, Joint Institute for Nuclear Research, Dubna, Russia, September 1-5, 1992, Los Alamos National Laboratory document LA-UR-92-3271.

R. P. Hjelm, P. Thiyagarajan, J. E. Epperson, R. K. Crawford, and J. M. Carpenter, "Comparison of SANS Instruments at Reactors and Pulsed Sources," International Seminar on Structural Investigation in Pulsed Sources, Joint Institute for Nuclear Research, Dubna, Russia, September 1-5, 1992, Los Alamos National Laboratory document LA-UR-92-3270.

R. P. Hjelm, J. Wilcoxon, P. Thiyagarajan, and H. Alkan, "Aqueous Mixed Colloids of Bile Salts and Phosphatidylcholines: A Problem with Many Length Scales," The 1992 Annual Meeting of the American Crystallographic Association, Pittsburgh, Pennsylvania, August 9-14, 1992, Los Alamos National Laboratory document LA-UR-92-1309.

R. Pynn, "Diffuse Neutron Scattering Signatures of Rough Films," in *Neutron Optical Devices and Applications*, C. F. Majkrzak and J. L. Wood, Eds. (The Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1992) Proc. SPIE Vol. 1738, pp. 270-281.

R. Pynn, "Probing Fine Magnetic Particles With Neutron Scattering," International Workshop on Studies of Magnetic Properties of Fine Particles and Their Relevance To Materials Science, Rome, Italy, November 4-8, 1991, Los Alamos National Laboratory document LA-UR-92-3851.

D. S. Sivia and **R. Pynn**, "Inverting Neutron Reflection Data," in *Neutron Optical Devices and Applications*, C. F. Majkrzak and J. L. Wood, Eds. (The Society of Photo-Optical Instrumentation Engineers, Bellingham, Washington, 1992) Proc. SPIE Vol. 1738, pp. 305-310.

G. S. Smith, "Neutron Reflectometry at a Pulsed Spallation Source," The 1992 Annual Meeting of the American Crystallographic Association, Pittsburgh, Pennsylvania, August 9-14, 1992, Los Alamos National Laboratory document LA-UR-92-3370.

J. Zhang, L. Eyring, and **R. B. Von Dreele**, "The Crystal Structures of Oxygen Deficient Rare Earth Oxides," The XVth Conference on Applied Crystallography, Ciescyn, Poland, August 9-12, 1992, Los Alamos National Laboratory document LA-UR-92-2601.

Beam Delivery

Published Articles

D. Neuffer, E. Colton, D. Fitzgerald, T. Hardek, R. Hutson, R. Macek, M. Plum, H. Thiessen, and T.-S. Wang, "Observations of a Fast Transverse Instability in the PSR," *Nuclear Instruments and Methods in Physics Research Section A* **321** (1-2), 1-12 (1992).

Publications in Press or Submitted

E. Bjorklund, M. Burns, G. Carr, S. Cohen, F. Naivar, S. Schaller, and R. B. Stuewe, "LAMPF-PSR Accelerator Complex Controls Upgrade: Architecture and Organization," Review of the Upgrade Plans for the LAMPF-PSR Accelerator Complex Control Systems, Los Alamos, New Mexico, February 25-27, 1992, Los Alamos National Laboratory document LA-UR-92-399

M. Burns, S. Cohen, M. Harrington, and S. Schaller, "LAMPF-PSR Accelerator Complex Controls Upgrade: Applications, Tools, and Diagnostics Review," Review of the Upgrade Plans for the LAMPF-PSR Accelerator Complex Control Systems, Los Alamos, New Mexico, February 25-27, 1992, Los Alamos National Laboratory document LA-UR-92-397.

N. Callaway, C. Burns, and M. Clay, "LAMPF-PSR Accelerator Complex Controls Upgrade: Operator Subcommittee Report," Review of the Upgrade Plans for the LAMPF-PSR Accelerator Complex Control Systems, Los Alamos, New Mexico, February 25-27, 1992, Los Alamos National Laboratory document LA-UR-92-298.

G. Carr, E. Bjorklund, S. Cohen, and D. Schultz, "LAMPF-PSR Accelerator Complex Controls Upgrade: Operator Interface," Review of the Upgrade Plans for the LAMPF-PSR Accelerator Complex Control Systems, Los Alamos, New Mexico, February 25-27, 1992, Los Alamos National Laboratory document LA-UR-92-394.

M. Plum, "Beam Dynamics and Beam Diagnostics at the Los Alamos Proton Storage Ring," Accelerator Physics Colloquium at the Relativistic Heavy Ion Collider, Brookhaven National Laboratory, Upton, New York, July 7, 1992, Los Alamos National Laboratory document LA-UR-92-2131.

R. B. Stuewe, E. Bjorklund, G. Carr, F. Naivar, S. Schaller, and D. Schultz, "LAMPF-PSR, Accelerator Complex Controls Upgrade: Front-End," Review of the Upgrade Plans

for the LAMPF-PSR Accelerator Complex Control Systems, Los Alamos, New Mexico, February 25-27, 1992, Los Alamos National Laboratory document LA-UR-92-395.

Contributed Conference Presentation

M. Burns, "A Distributed Design for Monitoring, Logging, and Replaying Device Readings at LAMPF," International Conference on Accelerator and Large Experimental Physics Control Systems, Tsukuba, Japan, November 11-15, 1991, Los Alamos National Laboratory document LA-UR-92-3539.

R. Macek, R. Thomas, and G. Stapleton, "Proceedings of the Workshop on the Use of Instrumentation and Probabilistic Safety Criteria for Prompt Radiation Protection at LAMPF, Volume I: Summaries, Discussion, Conclusions, and Recommendations," Los Alamos, New Mexico, December 9-11, 1991, Los Alamos National Laboratory document LA-UR-92-300.

M. Plum, M. Borden, R. Hutson, W. Sommer, and P. Ferguson, "Thermocouple Measurements of High-Current Beam Profiles," Spring Meeting for the American Physical Society, Washington, D.C., April 20-24, 1992, Los Alamos National Laboratory document LA-UR-92-18.

K. Scarborough and S. Cohen, "Beam Position Monitor Upgrade at the LAMPF Proton Storage Ring," The International Conference on Accelerator and Large Experimental Physics Control Systems, Tsukuba, Japan, November 11-15, 1991, Los Alamos National Laboratory document LA-UR-92-3540.

S. Schaller, R. Stuewe, E. Bjorklund, M. Burns, T. Callaway, G. Carr, S. Cohen, M. Harrington, D. Kubicek, R. Poore, and D. Schultz, "Experience Controlling the LAMPF-PSR Accelerator Complex," The International Conference on Accelerator and Large Experimental Physics Control Systems, Tsukuba, Japan, November 11-15, 1991, Los Alamos National Laboratory document LA-UR-92-3608.

R. Stuewe, S. Schaller, E. Bjorklund, M. Burns, T. Callaway, G. Carr, S. Cohen, D. Kubicek, M. Harrington, R. Poore, and D. Schultz, "Future Directions in Controlling the LAMPF-PSR Accelerator and Beam Delivery Complex at Los Alamos National Laboratory," The International Conference on Accelerator and Large Experimental Physics Control Systems, Tsukuba, Japan, November 11-15, 1991, Los Alamos National Laboratory document LA-UR-92-3608.

H. A. Thiessen, "LAMPF-Intense Spallation Source and PILAC," Third Generation Spallation Source Workshop, Kernforschungsanlage (KFA), Juelich, Germany, Los Alamos National Laboratory document LA-UR-92-2443.

Publications by Nuclear Physics PRTs

Published Articles

C. M. Frankle, C. D. Bowman, J. D. Bowman, S. J. Seestrom, E. I. Sharapov, Yu. P. Popov, and N. R. Roberson, "Neutron Resonance Spectroscopy on ^{113}Cd : The p-wave levels," *Physical Review C* **45**, 2143-2146 (1992).

C. M. Frankle, J. D. Bowman, J. E. Bush, P. P. Delheij, C. R. Gould, D. G. Haase, J. Knudson, G. E. Mitchell, S. Penttila, H. Postma, N. R. Roberson, S. J. Seestrom, J. J. Szymanski, S. H. Yoo, V. W. Yuan, and X. Zhu, "Parity Nonconservation for Neutron Resonances in ^{232}Th ," *Physical Review C* **46**, 778-787 (1992).

C. M. Frankle, J. D. Bowman, J. E. Bush, P. P. Delheij, C. R. Gould, D. G. Haase, J. Knudson, G. E. Mitchell, S. Penttila, H. Postma, N. R. Roberson, S. J. Seestrom, J. J. Szymanski, V. W. Yuan, and X. Zhu, "Parity Nonconservation for the 0.88-eV Neutron Resonance in ^{81}Br ," *Physical Review C* **46**, 1542-1545 (1992).

D. G. Haase, J. D. Bowman, P. P. Delheij, C. M. Frankle, C. R. Gould, J. N. Knudson, J. E. Koster, G. E. Delheij, C. M. Frankle, C. R. Gould, D. G. Haase, J. N. Knudson, S. Penttila, H. Postma, N. R. Roberson, S. J. Seestrom, J. J. Szymanski, S. H. Yoo, V. W. Yuan, and X. Zhu, "Parity Nonconservation for Neutron Resonances," The 21st International Symposium on Nuclear Physics, 1992.

Invited Talks

S. J. Seestrom, C. D. Bowman, J. D. Bowman, J. N. Knudson, R. Mortensen, S. Penttila, J. J. Szymanski, S. A. Wender, S. H. Yoo, V. W. Yuan, C. M. Frankle, C. R. Gould, D. G. Haase, G. E. Mitchell, N. R. Roberson, X. Zhu, P. P. Delheij, H. Postma, E. I. Sharapov, and Yu. P. Popov, "Measurement of Parity Violation in Neutron-Nucleus Reactions," *Intersections between Particle and Nuclear Physics*, W. T. H. van Oers, Ed. (American Institute of Physics, Salem, Massachusetts, 1992), Vol. 243, pp. 40-52.

Author index

<i>Author</i>	<i>Proposal No.</i>	<i>Page</i>	<i>Author</i>	<i>Proposal No.</i>	<i>Page</i>
Abrams, L.	5153	76	Costanzo, P. M.	5013	24
Allison, J. E.	5122	74	Dai, L.	5155	162
Anastasiadis, S.	5038	152	Davies, P. K.	5065	32
Aranda, M. A. G.	5133	42	Dixon, R.	5069	64
Argyriou, D. N.	5020	92	Dotson, L.	5054	182
Attfield, P.	5133	42		5130	184
Baker, S.	5025	140	Dreux, P.	5103	116
	5026	144	Durham, W. B.	5075	68
	5118	160	Eckert, J.	5054	182
	5138	174		5130	184
	5704	172		5159	190
Ball, R. C.	5155	162		5160	186
Barford, W.	5155	162	Egami, T.	5116	38
Barger, W.	5025	140	Elcombe, M. M.	5020	92
Barthes, M.	5159	190	Eyring, L.	5092	70
Bassereau, P.	5085	149	Field, J. B.	5155	162
Bennett, K.	5047	96	Fillaux, F.	5054	182
	5074	66	Fischer, J. E.	5116	38
	5075	68	Fitzsimmons, M. R.	5081	154
Berkowitz, A.	5137	166		5112	158
Berman, A.	5118	160		5137	166
Besson, J. M.	5146	44		5702	104
Billinge, S. J. L.	5052	30	Foreman, L. R.	5411	168
	5066	34	Forsman, W. C.	5103	116
	5116	38	Franzen, H. F.	5077	36
Bish, D. L.	5013	24	Garzon, F. H.	5065	32
de Boer, F. R.	5001	18	Giese, Jr., R. F.	5013	24
	5004	20	Gill, R.	5038	152
Brosha, E. L.	5065	32	Glausinger, W. S.	5129	40
Bourke, M. A. M.	5059	62		5130	184
	5069	64	Goldstone, J. A.	5002	56
	5074	66		5046	28
	5075	68		5059	62
	5122	74		5069	64
	5701	82		5075	68
Bruck, E.	5001	18		5122	74
Bruque, S.	5133	42		5129	40
Burkel, E.	5081	154		5169	78
Buschow, K. H. J.	5002	56		5400	80
	5004	70		5405	46
Bussmann, K.	5012.1	60		5701	82
Bussod, G. Y.	5047	96	Goodenough, J. B.	5012.1	60
Butler, P.	5026	144	Gratz, A. J.	5074	66
Cachet, C.	5054	182	Gray III, G. T.	5059	62
Candler, R. J.	5411	168	Hadziioannou, G.	5038	152
Canfield, P. C.	5037	24	Hamel, G.	5146	44
Carrey, M.	5137	166	Hamilton, W.	5026	144
Cline, J. P.	5035	23		5155	162
Cooper, E. A.	5702	104	Hanley, H. J. M.	5010	22
Corbin, D.	5153	76	Harrison, W. T. A.	5000	54
Cort, B.	5400	80		5012.1	60
	5405	46	Havela, L.	5004	20
Cost, J.	5404	132	Hayter, J.	5026	144

<i>Author</i>	<i>Proposal No.</i>	<i>Page</i>	<i>Author</i>	<i>Proposal No.</i>	<i>Page</i>
Heidelberg, F.	5048	98	Martino, T.	5140	122
Hellstrom, E. E.	5090	100	Matthies, S.	5046	28
Hjelm, R. P.	5071	117	Mayes, A. M.	5084	156
	5404	132		5085	149
Hoffer, J. K.	5411	168		5108	120
Hubbard, K.	5704	172	Nakotte, H.	5001	18
Israelachvili, H.	5118	160		5004	20
Jacobson, A. J.	5000	54	Nastasi, M. A.	5112	158
	5012	58		5704	172
	5012.1	60	Nelmes, R. J.	5091	102
James, M. R.	5701	82		5146	44
Janulis, E. P.	5127	163	Nenoff, T. M.	5153	76
Jayasooriya, U. A.	5168	188	Newnham, R. E.	5098	72
Johnson, S. W.	5159	190	Olah, G. A.	5058	114
Jones, G.	5153	76	Olivier, B. J.	5049	112
Kalceff, W.	5035	23		5052	30
Kearley, G. J.	5054	182	Ong, E. W.	5129	40
Kent, M. S.	5700	170		5130	184
Kirby, S. H.	5075	68		5160	186
Klotz, S.	5146	44		5169	78
Kuhl, T.	5118	160	Ouboumour, H.	5054	182
Kumar, S.	5023	110	Parise, J. B.	5153	76
Küppers, Horst	5160	186	Peisl, J.	5081	154
Kwei, G. H.	5066	34	Penfold, W.	5155	162
	5116	38	Pickering, I. J.	5000	54
Larson, A. C.	5040	94	Powell, A. K.	5168	188
	5046	28	Purwanto, A.	5001	18
	5047	96		5004	20
	5048	98		5037	26
	5090	100	Pynn, R.	5137	166
	5091	102		5138	174
	5702	104	Raistrick, I. D.	5065	32
Lawson, A.C.	5002	56	Ramakrishna, B. L.	5169	78
	5052	30	Reiker, T. P.	5023	110
	5059	62		5127	163
	5069	64	Reinen, D.	5169	78
	5075	68	Reis, K. P.	5012	58
	5122	74	Robinson, R. A.	5001	18
	5400	80		5002	56
	5404	132		5004	20
	5405	46		5037	26
	5701	82	Robl, C.	5019	90
Lewandowski, J. T.	5000	54	Rokop, S.	5058	114
Liu, X.	5118	160	Rossetti, Jr., G. A.	5098	72
	5137	166	Russell, T. P.	5084	156
Loveday, J. S.	5091	102		5085	149
	5146	44		5108	120
Macias, F.	5071	117		5148	128
Maddaford, P.	5151	130	Sabine, T. M.	5035	23
Magid, L.	5026	144	Salazar, M.	5411	168
Mang, J. T.	5023	110	Schmitt, F.-J.	5118	160
Margulies, D.	5137	166	Sechovsky, V.	5004	20
Marking, G.	5077	36	Seeger, P.	5049	112
Martinez, R.	5404	132		5071	117

<i>Author</i>	<i>Proposal No.</i>	<i>Page</i>
Seeger, P.	5404	132
Shi, N.	5122	74
Sickafus, K. E.	5702	104
Smith, G. S.	5026	144
	5081	154
	5112	158
	5118	160
	5127	163
	5137	166
	5138	174
	5155	162
	5700	170
	5704	172
Smyth, J. R.	5040	94
Snow, A.	5025	140
Sorenson, C.M.	5049	112
Stanley, H.	5155	162
Steinberg, S.	5118	160
Stout, M. G.	5069	64
	5122	74
Straty, G. C.	5010	22
Stuckey, G. D.	5153	76
Swope, R. J.	5040	94
Takagi, H.	5066	34
Thiyagarajan, P.	5071	117
Thompson, J. D.	5037	26
Toprakcioglu, C.	5038	152
	5151	130
	5155	162
Trehwella, J.	5058	114
Von Dreele, R. B.	5035	23
	5046	28
	5052	30
	5092	70
	5129	40
	5146	44
	5153	76
	5405	46
Wenk, H.-R.	5046	28
	5047	96
	5048	98
	5075	68
Wilcoxon, J.	5140	122
Wilson, R. M.	5091	102
	5146	44
Yoshizawa, H.	5118	160
Young, V.	5077	36
Yu, L. T.	5054	182
Zhang, J.	5092	70
Zocco, T. G.	5404	132

Subject index

<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>	<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>
Aluminum titanium carbide	5122	74	Copolymer	5155	162
Absorption theory	5035	23		5700	170
Acetanilide	5159	190	Copper	5001	18
Actinide elements	5400	80		5059	62
Air surface	5700	170		5065	32
Alignment	5090	100		5066	34
Aluminosilicate	5153	76		5169	78
Aluminum	5001	18	Cryostat	5411	169
	5122	74		5004	21
	5701	82	Cryptate	5019	90
Ammonia	5130	184	Crystal structure	5000	54
Anemometry	5026	145		5001	18
Annealing	5084	156		5004	20
Arsenic	5133	42		5012.1	60
	5153	76		5013	24
Atomic diffusion	5704	172		5020	92
Beryllium arsenic oxide	5153	76		5040	94
Beryllium phosphorus oxide	5153	76		5047	96
BSCCO wire	5090	100		5054	182
Barium	5012	58		5091	102
	5065	32		5133	42
	5066	34		5169	78
Barium-copper oxide binary system	5065	32	Curie-Weiss magnetic behavior	5012.1	60
Beryllium	5069	64	D-polystyrene	5038	152
	5153	76	Debye-Bueche model	5023	110
Beta-layering	5411	168	Debye-Waller factors	5405	46
Biomineralisation	5168	188	Deformation	5047	96
Binary liquid mixtures	5010	22		5048	98
Biotite	5048	98	Dektak machine	5137	166
Bismuth	5012	58	Density profile	5025	140
Boron	5146	44		5026	144
	5704	172		5103	116
Boundary Effects	5127	163		5118	161
Bragg pattern	5122	74		5155	162
	5169	79	Dewetting	5084	156
Cesium rhodium silicate	5037	26	Difference fourier	5020	92
Calcium-ammonia intercalate	5130	184		5013	24
Calcium-ammonia solvation	5129	40	Difference nuclear density map	5020	92
Calcium concentration	5130	184	Dupont LUDOX HS-30	5071	117
Carbon	5116	38	Equation of state	5146	44
	5138	174	Extinction theory	5035	23
	5122	74	Ferrite	5137	166
Cation	5012	58	Ferritin	5168	188
Cesium	5037	26	Ferroelectrics	5098	72
Chromites	5169	78	Flipping ratio	5081	155
CLIMAX	5168	189		5137	166
Contrast variation	5071	118	Flourination	5127	163
	5151	130	Fourier	5116	38
Copolymer	5038	152		5133	42
	5084	156		5405	46
	5085	149	Gallate compositions	5153	76
	5108	120	Gallium	5052	30
			Gas gun	5074	66

<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>	<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>
Gel point	5049	112	Lead	5012	58
Generalized Structure Analysis System (GSAS)	5000	54	Lead titanate	5098	72
	5001	18	Liquid crystal	5127	163
	5020	92	LiMnXO ₄	5133	42
	5046	28	Lithium	5133	42
	5077	36	Lithium nickel oxide	5000	54
	5129	40	Magnesium	5081	154
	5146	45	Magnesium oxide	5081	154
	5169	78	Magnetic properties	5004	20
	5405	46		5081	154
Germanium	5004	20		5112	158
Goniometer	5148	128		5137	166
Granite	5048	98	Magnetic structure	5112	158
Guinier analysis	5140	123		5169	78
η -Pu _{0.90} Np _{0.10}	5400	80	Manganese	5133	42
Hafnium	5077	36	Manganese dioxide	5054	182
Heavily deformed in-situ composites (HDISC)	5059	62	Maximum entropy reconstruction	5160	187
Heteropolytungstate	5019	90	Metal matrix composites	5701	82
Homopolymer	5038	152	Microemulsions	5140	122
	5084	156		5151	130
Hydrogen bond	5013	24	Microscopy	5098	73
	5019	90		5035	23
	5160	186	Molybdenum	5701	82
Ice	5074	66	Mössbauer spectroscopy	5137	166
	5075	68	Mott-Hubbard insulator	5012.1	60
Infrared	5168	189	Ni _{0.18} Cu _{0.82} Cr ₂ O ₄	5169	78
Interface properties	5025	140	Ni _{0.82} Cu _{0.18} Cr ₂ O ₄	5169	78
	5084	156	Néel point	5002	56
	5038	152	Neptunium	5400	80
	5069	64	Newtonian fluid	5026	144
	5103	116	Nickel	5081	154
Ion exchange	5153	77		5169	78
Iridium	5004	20	Niobium	5059	62
Iron	5168	188		5701	82
	5112	158	Non-Newtonian fluid	5026	144
Jahn-Teller effects	5169	78	Nuclear reaction analysis	5038	153
Kaolinite	5013	24	Olivine	5047	96
Landau-Ginzberg approach	5151	130	Omega West	5702	104
Langmuir-Blodgett technique	5025	140	Optical microscopy	5127	165
	5118	160	Order-disorder transition	5091	102
	5137	167		5108	120
Langmuir trough	5025	141	Ornstein-Zernike model	5023	110
Lanthanum	5066	34		5151	130
Lanthanum cuprate	5066	34	Oxygen nonstoichiometry	5012	58
Lanthanum titanate	5098	72	Praseodymium oxide	5092	70
Laser ablation	5138	174	Pair distribution	5066	34
Laser interferometry	5138	174		5116	38
Lattice orientation	5048	98	Paris-Edinburgh cell	5146	44
	5702	104	Particle size	5054	182
Lattice voids	5404	132	Peierl's stress	5059	63
Laue technique	5091	102	Perovskite	5098	73
			Perovskite oxides	5012	58
			Phase behavior	5023	110

<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>	<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>
Phase behavior	5074	66	Rietveld analysis	5146	44
	5108	120		5153	77
	5140	122	Rubidium	5116	38
Phosphorus	5153	76	Rutile	5040	94
Phthalocyanine	5025	140	Sapphire	5138	174
Plutonium	5400	80	Shear stress	5026	144
	5404	132	Shear cell	5026	144
	5405	46	Siemens single crystal		
Polarized neutrons	5112	158	diffractometer	5040	95
Poly(dimethyl aminoethyl			Side chain	5023	110
methacrylate)	5103	116	Silicon	5037	26
Poly(dimethyl) siloxane	5700	170	Silver	5090	100
Poly(ethylene-oxide)	5118	160	Small angle neutron scattering	5103	116
Poly(metha)acrylate	5023	110		5108	120
Poly(n-butyl methacrylate)	5103	116		5148	128
	5108	120		5151	130
Polymer	5023	110		5404	132
	5038	152	Spin flipper	5112	158
	5085	149	Squaric acid	5091	102
	5103	116	Stearic acid	5137	166
	5148	128	Stoichiometry	5137	166
	5155	162	Strain	5059	62
Polystyrene	5049	112		5069	64
	5108	120		5075	68
	5148	128		5122	74
	5026	146		5701	82
Poly(styrene-b-methyl			Stress	5059	62
methacrylate)	5084	156		5122	74
	5085	149		5701	82
Poly(vinyl-2-pyridine)	5038	152	Stress rig	5122	74
Porod law	5140	123	Structural properties	5004	20
Praseodymium	5092	70		5010	22
Pressure	5037	26		5025	140
Pressure cell	5037	26		5038	152
	5146	44		5049	112
Proton dynamics	5054	182		5065	32
Quartz	5048	98		5081	154
Quinolinic acid	5160	186		5092	70
Rb ₃ C ₆₀	5116	38		5116	38
RHO	5153	76		5118	160
Radial distribution	5052	30		5151	130
Radiography	5411	168		5700	170
Rhodium	5037	26		5153	76
Rietveld analysis	5000	54	Structural distortion	5002	56
	5002	56	Stuhrmann plot	5058	114
	5012.1	61	Sulfur	5077	36
	5046	28	Surface profilometry	5127	165
	5066	34	Surface roughness	5085	149
	5069	65	Surface structure	5026	144
	5077	37	Surfactants	5118	160
	5092	70		5137	166
	5098	72	Tantalum	5077	36
	5116	38	Temperature dependence	5159	190
	5129	40	Texture analysis	5075	68
	5133	42			

<i>Subject</i>	<i>Proposal No.</i>	<i>Page</i>
Texture analysis	5046	28
Thallium	5153	76
Thermal expansion	5400	80
Thin film	5025	140
	5081	154
	5112	158
	5148	128
Time of flight	5012	58
	5035	23
	5071	117
	5075	68
	5091	102
	5704	172
Titanium	5069	64
	5122	74
	5701	82
Titanium disulfide	5129	40
	5130	184
Tritium	5411	168
Troponin complex	5058	114
Twist grain boundaries	5081	154
UCu ₃ Al ₂	5001	18
UIrGe	5004	20
UPdSn	5002	56
Uranium	5001	18
Vacuum furnace	5153	77
Vanadium	5138	174
	5701	82
Vibrational modes	5130	184
	5160	186
	5169	78
Wetting	5138	174
X-ray	5085	150
	5040	95
	5065	32
	5098	72
	5108	120
	5169	78
YAG	5702	104
Zinc vanadium oxide	5012.1	60
Zirconia	5020	92

**DATE
FILMED**

6/3/94

END