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*The Manuel Lujan, Jr.
Neutron Scattering Center
LANSCE Experiment Reports
1990 Run Cycle*

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*Compiled by
Maria A. DiStravolo*

Los Alamos
NATIONAL LABORATORY

Los Alamos, New Mexico 87545

MASTER

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**The Manuel Lujan, Jr. Neutron Scattering Center
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1990 Run Cycle**

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ABSTRACT

This year was the third 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 facility, which results in LANSCE spectrometers being available to external users for unclassified research about 80% of each six-month 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 thirty-four proposals were submitted for unclassified research and twelve proposals for research of a programmatic nature to the Laboratory. Oversubscription for instrument beam time by a factor of two was evident with 592 total days requested and only 278 available for allocation.

Our definition of beam availability is when the proton current from the PSR exceeds 50% of the planned value. The PSR ran at 65 μ A current (average) at 20 Hz for most of 1990. The overall beam availability averaged as follows:

- 60% during cycle 56 (May 27 to July 4)
- 79% during cycle 57 (July 21 to August 26)
- 69% during cycle 58 (September 7 to October 17)

All of the scheduled experiments were performed (excluding those few withdrawn because of problems with samples), and experiments in support of the LANSCE research program were accomplished during the discretionary periods.

**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 6 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 - 6.0 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	0.02 - 4 cm ³
Experiment duration	5 minutes - 1 day, depending on sample size

Robert Von Dreele, instrument scientist

John Thomas, instrument technician

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>												
HIPD	A. C. Lawson	3302												
Title:		Report received: <i>(for LANSCE use only)</i>												
Magnetic and Structural Properties of Uranium ternaries with the CeCu ₂ Structure: UPtGe		1/8/91												
Authors and affiliations:														
<p>R. A. Robinson, LANSCE, LANL A. C. Lawson, MST Division, LANL K. H. J. Buschow, Philips Research Labs., Eindhoven</p>														
Experiment report:														
<p>The idea of this experiment was to determine the crystallographic and magnetic structure of UPtGe, which was thought to crystallise in the CeCu₂ structure type with space group Imma. UPtGe is one of a series of UTGe compounds that have been characterised by means of magnetic susceptibility, electrical resistivity and specific heat measurements[1,2]. In going from T = Co, Ru, which are non-magnetic, through T = Rh, which is a weak ferromagnet, to T = Pd, Ni, Pt, which appear to exhibit complicated types of 5f-moment ordering, one proceeds from itinerant to localised behaviour, presumably as a function of the gradual reduction of 5f-d hybridisation. UPtGe was thought to order antiferromagnetically at 51K and we therefore made neutron diffraction measurements at room temperature, 75K and 15K.</p> <p>The 75K data refines well to the NiSiTi structure type (with space group Pnma) which is the ordered form of the CeCu₂ structure. The refined parameters are as follows:</p> <p>Lattice parameters: $a = 7.1856 \text{ \AA}$, $b = 4.3286 \text{ \AA}$, $c = 7.5146 \text{ \AA}$</p> <table> <tr> <td>U</td> <td>at x, 1/4, z</td> <td>x = -0.0004</td> <td>z = 0.2157</td> </tr> <tr> <td>Pt</td> <td>at x, 1/4, z</td> <td>x = 0.2101</td> <td>z = 0.5907</td> </tr> <tr> <td>Ge</td> <td>at x, 1/4, z</td> <td>x = 0.7833</td> <td>z = 0.5809</td> </tr> </table> <p>The diffraction patterns in one of the 40° detector banks, taken above and below T_N, are shown in the Figure. There are number of extra peaks in the low temperature pattern, most notably at the strong peaks at 5.9 Å and 7.8 Å. We presume that they are magnetic in origin. So far we have been unable to find a simple indexing scheme. It is entirely possible that the magnetic structure is incommensurate: some of the isostructural rare-earth-based compounds are known to exhibit quite complicated helical structures[3]</p>			U	at x, 1/4, z	x = -0.0004	z = 0.2157	Pt	at x, 1/4, z	x = 0.2101	z = 0.5907	Ge	at x, 1/4, z	x = 0.7833	z = 0.5809
U	at x, 1/4, z	x = -0.0004	z = 0.2157											
Pt	at x, 1/4, z	x = 0.2101	z = 0.5907											
Ge	at x, 1/4, z	x = 0.7833	z = 0.5809											

Experiment report (continued):

Figure. Portions of diffraction patterns from UPtGe, taken at 75K and 15K respectively in one of the 40° banks on HIPD. The extra peaks in the low-temperature pattern, which are presumed to be magnetic, are marked with the symbol "M"

References:

- [1] K. H. J. Buschow, E. Brück, R. G. van Wierst, F. R. de Boer, L. Havela, V. Sechovsky, P. Nozar, E. Sugiura, M. Ono, M. Date and A. Yamagishi, J. Appl. Phys. 67, 5215 (1990).
- [2] B. Chevalier, B. Lloret, P. Gravereau, B. Buffat and J. Etourneau, J. Magn. Magn. Mater. 75, 13 (1988).
- [3] W. Bazela, J. Leciejewicz and A. Szytuła, J. Magn. Magn. Mater. 50, 19 (1985).

Instrument used: <i>(please type)</i> HIPD	Local contact: A. C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 3303
Title: Magnetic and Structural Properties of Uranium-based Heusler Alloys: URhSb		Report received: <i>(for LANSCE use only)</i> 2/6/91
Authors and affiliations: R. A. Robinson, LANSCE, LANL A. C. Lawson, MST Division, LANL K. H. J. Buschow, Philips Research Labs., Eindhoven		
Experiment report: The idea of this experiment was to observe magnetic diffraction in the U-based Heusler alloy URhSb. We had previously studied[1] the isostructural alloy UNiSn, which orders in the FCC Type I antiferromagnetic structure, with a moment of $1.42\mu_B$ parallel to the [100] axis. On the basis of susceptibility measurements[2], it was thought that URhSb ordered antiferromagnetically at 40K. We set out to observe this directly using neutron diffraction on HIPD. We took data sets at 300K, 65K and 15K and confirmed that URhSb crystallises in the MgAgAs or $C1_b$ structure type, with a lattice parameter of $6.5213\text{\AA}$ at 65K. U is on the $(1/2, 1/2, 1/2)$ site, Rh on $(3/4, 3/4, 3/4)$ and Sb on $(0, 0, 0)$. Thus, U is on the same site that Mn occupies in the regular Heusler alloys. There were no signs of magnetic ordering; if one assumes the same Type I FCC antiferromagnetic structure with moments parallel to [001] (the magnetic structure that UNiSn exhibits[1]), our data indicate that the uranium moment must be less than $0.03\mu_B$.		

Experiment report (*continued*):

References:

- [1] M. Yethiraj, R. A. Robinson, J. J. Rhyne, J. A. Gotaas and K. H. J. Buschow, J. Magn. Magn. Mater. 79, 355 (1989).
- [2] T. T. Palstra, G. J. Niewenhuys, R. F. M. Vlastuin, J. van den Berg, J. A. Mydosh and K. H. J. Buschow, J. Magn. Magn. Mater. 67, 331 (1987).

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
HIPD	A. C. Lawson	3304.0
Title: Magnetic and Structural Properties of Tetragonal VPt ₃		Report received: <i>(for LANSCE use only)</i> 1/31/91
Authors and affiliations: R. A. Robinson, LANSCE, LANL A. C. Lawson, MST Division, LANL K. H. J. Buschow, Philips Research Labs., Eindhoven		
Experiment report: <p>The idea of this experiment was to determine the magnetic structure of tetragonal VPt₃. VPt₃ can be made in three structures: Cu₃Au (cubic), TiAl₃ (tetragonal) and disordered (FCC). Jesser et al. [1] have reported that The TiAl₃ phase orders magnetically at a temperature of 210K, with a saturation moment of 0.1μ_B per formula unit. They interpret this as being due to itinerant magnetism., but it seems very strange to have such small moments with such a large T_C. On the other hand there is some evidence from NMR experiments [2] and the trend in other alloys [3] that one might have a moment of 1.0μ_B on the vanadium site and an opposing moment of 0.3μ_B on each of the Pt sites. We set out to observe this and thereby distinguish between the two models.</p> <p>The sample consisted of two solid pieces, which were so ductile that they could not easily be ground. The TiAl₃ superlattice lines were however observed in a surface X ray diagram. Prior to the neutron diffraction experiment, we also made susceptibility measurements in a Squid magnetometer. These indicated that our sample ordered at approximately 113K, with a very small saturation moment at low temperature of 0.00023 μ_B per formula unit. Above the transition, the susceptibility could not readily be interpreted using the Curie-Weiss formula.</p> <p>Nevertheless, we proceeded with the neutron experiments at temperatures of 300K and 10K. Unfortunately, there were significant differences between banks of equivalent detectors. We presume these to be due to a relatively large grain size and significant preferred orientation. There are no extra lines in the 10K pattern, beyond those in the 300K pattern, not that we would expect any. In the 300K pattern, part of which is shown in the Figure, there is a set of sharp (resolution-limited) lines that index to the TiAl₃ structure (rather than the other reported phases). However, there are also many other lines which are broadened considerably. They do not correspond to any of the intermetallic V-Pt compounds catalogued[4]. We note that a variety of long period superstructures[5] have been observed by means of electron microscopy in V-Pt alloys near the composition 1:3, and most of the remaining lines can be indexed within a structure with an 8-fold stacking sequence. This structure has a stacking sequence of ABABBABA, where each letter refers</p>		

Experiment report (continued):

to one V-Pt plane. The TiAl_3 structure corresponds to AB stacking. There is some evidence that there is a significant magnetic component to the 002 (in the TiAl_3 indexing) reflection, but it is not consistent from detector bank to detector bank. Taking average values, assuming that the moments lie in the tetragonal plane and that the total moment is zero, in accordance with the susceptibility data, we obtain moments of $\mu_V \sim 0.6 \mu_B$ and $\mu_{Pt} \sim -0.2 \mu_B$.

We now intend to grind the sample to powder, anneal it again and repeat the susceptibility and neutron diffraction experiments.

Figure: Part of diffraction pattern for VPt_3 at 300K in one of the 153° banks. The upper markers correspond to the TiAl_3 structure, while the lower ones correspond to the 8-fold stacking sequence. The calculated intensities do not agree very well with observation, presumably because of preferred orientation.

References:

- [1] R. Jesser, A. Rieber and R. Kuentzler, J. de Physique 44, 631 (1983).
- [2] M. Kawakami and T. Goto, J. Phys. Soc. Japan 46, 1492 (1979).
- [3] S. J. Pickart and R. Nathans, J. Appl. Phys. 34, 1203 (1963).
- [4] P. Villars and L. D. Calvert, "Pearson's Handbook of Crystallographic Data for Intermetallic Phases", Vol. 3, American Society for Metals (Metals Park, OH) (1985).
- [5] D. Schryvers and S. Amelinckx, Mat. Res. Bull. 20, 367 (1985) and references therein.

Experiment report (continued):

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: A. C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 3310
Title: TEXTURE of CROSS-ROLLED TITANIUM METAL		Report received: <i>(for LANSCE use only)</i> 1/18/91
Authors and affiliations: A. C. Lawson, G. T. Gray III, J. Vaninetti and G. Danner, MST-5 D. Viskoe and T. Claytor, WX-3 D. Sivia, T-11 and LANSCE A. Cheng and J. A. Goldstone, LANSCE Los Alamos National Laboratory Los Alamos NM 87545		
Experiment report: <p>We have been using the High Intensity Powder Diffractometer (HIPD) to determine metallurgical textures in large (2-10 cm) samples. The advantage of using neutrons for these measurements is that the bulk of the sample rather than just the surface is measured. The experimental setup is shown schematically in Fig. 1. This figure, which is not to scale, shows a plan view of the diffractometer, the detectors, the corresponding diffraction vectors, an edge-view of a coin-shaped sample, and the axis normal to the sample. Provision is made for rotating the sample axis in the plane of the diffractometer and for rotating the sample about its axis. These motions can be pre-programmed to allow automatic data collection.</p> <p>Our sample was a disk of α-titanium of dimensions diameter = 2" and thickness = 3/16". The material had been cross-rolled in the plane of the disk to produce a sample initially believed to have cylindrical symmetry about the axis of the disk. We used a 2" x 1/2" rectangular beam to collect about forty data sets of different sample orientations during about 12 hours beam time. In principle, such data contains a set of inverse pole figures that should be sufficient for the determination of the Orientation Distribution Function (ODF). We have been planning to perform the necessary data reduction by use of the Maximum Entropy technique; however, work on the required software has not been completed. To effect a preliminary data reduction, we have combined data from different orientations with the assumption of cylindrical symmetry of the sample to produce selected direct axial distribution functions. Some of the results are shown in the Figs. 2 and 3.</p> <p>Fig. 2 shows the distribution of (0001) poles as a function of polar angle (α). These data are taken for a particular value of the azimuthal angle, $\beta = 0^\circ$, and show data combined from four different detector banks after appropriate corrections. The peak at about 20° is in agreement with published pole figures of</p>		

zirconium. Fig. 3 shows the distribution of (0001) poles as a function of azimuthal angle β for various values of the polar angle α . This figure shows that the assumption of cylindrical symmetry is only approximately satisfied. Space does not permit the display of several other distribution functions that were also calculated.

This experiment shows that satisfactory data can be collected on large samples using pulsed neutron diffraction on a powder diffractometer. Data analysis techniques for such experiments unfortunately remain in a rudimentary state.

Figure 1

Figure 2

Figure 3

Instrument used: <i>(please type)</i> HIPD	Local contact: A. C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 3312
Title: ATTEMPT to OBSERVE TEXTURE in α -PLUTONIUM		Report received: <i>(for LANSCE use only)</i> 12-7-90
Authors and affiliations: <p>D. Eash, C. Olsen and B. Cort, NMT-5 A. C. Lawson, MST-5 Los Alamos National Laboratory Los Alamos NM 87545</p>		
Experiment report: <p>Following the recognition of the orientation relation between α-020 and δ-111 for the α- and δ-phases of plutonium metal [1], it seemed worthwhile to devise an experiment that would trace the orientation relations through <u>all</u> the phases of plutonium. A successful experiment of this kind would provide valuable information about the transformation behavior of this extremely complicated material.</p> <p>As a preliminary step in this direction, we have attempted to determine the 020-texture in a specially prepared sample of α-plutonium. The sample was prepared by the compressive loading method of Bronisz and Tate [2]. Our implementation of this preparation method was expected to produce a right circular cylinder of dimensions 1/4" x 2" having needle shaped α-grains with 020 oriented normal to both grain and cylinder axes. This symmetrical situation is ideally suited to the preferred orientation formalism that is routinely available in our Rietveld refinement package (GSAS.) Some difficulty was encountered during the preparation, and it is estimated that only about half the sample received the correct treatment.</p> <p>Diffraction patterns of the doubly encapsulated sample were obtained on the High Intensity Powder Diffractometer (HIPD). The data were refined using GSAS, and the results for the +153° detector bank are shown in the accompanying figure.</p> <p>It was found that the sample contained 10% δ-phase, but no significant preferred orientation was observed for the α-phase. We do not understand the reasons for this failure, and it remains to undertake a metallographic examination of our sample to determine whether the expected state of orientation was achieved.</p>		

Experiment report (continued):

ALPHA PLUTONIUM TEXTURE - 305 K

BANK 1, 2-THETA 153.4, L-S CYCLE 116 OBSD. AND DIFF. PROFILES

References:

- [1] C. E. Olsen, J. Nuc. Mat. 168 326 (1989).
- [2] S. E. Bronisz and R. E. Tate, Trans. AIME 233 1396 (1965).

Instrument used: <i>(please type)</i> HIPD	Local contact: R. B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5315
Title: Structures of the Three Phases of PaD_x		Report received: <i>(for LANSCE use only)</i> 1/8/91
Authors and affiliations: John W. Ward, B. Cort, John M. Haschke, A. C. Lawson, and R. B. Von Dreele, Los Alamos National Laboratory J. C. Spirlet, European Institute for Transuranium Elements		
Experiment report: <p>Protactinium forms three distinct hydride phases. Two of these are isomorphous to structures also found in the uranium hydride system. These are the $\alpha\text{-UD}_3$ structure in which the uranium atoms occupy a bcc lattice, and $\beta\text{-UD}_3$, in which the uraniums occupy an A15 lattice. The third allotrope of PaD_x forms as a C15 Laves phase, a unique structure in binary hydrides. The location of the deuteriums is not known with certainty for any of the protactinium hydrides, and the description given here is based on analogy to the better-known UD_3 system.</p> <p>Both the A15 and C15 structures are characteristic of <i>transition metal intermetallic</i> compounds. Their appearance in the actinide hydrides is most surprising, as a metal playing a dual role without an apparent valence difference is unknown elsewhere. The effect is clearly due to the appearance of broadband, bonding 5f electrons. It is therefore of great interest to know the structures of these compounds.</p> <p>After preliminary experiments with a rare, 1.5-g sample of protactinium in 1989, we made two more attempts to prepare hydride samples of protactinium for the 1990 run cycle. We used several hydride/dehydride cycles to insure that the sample hydrided completely, and we used a sample holder with smaller diameter and thinner walls to reduce the contribution of the vanadium</p>		

Experiment report (continued):

to the diffraction pattern. Consequently, the quality of the data was very much improved over 1989. However, neither of the two hydride compositions was made successfully, apparently because of contamination of the sample with a large fraction of PaO, which presumably formed during handling, despite our precautions. The diffraction pattern for the second attempt, shown in the figure, shows protactinium oxide and metal; no hydrogen is detectable. We conclude that the sample will have to be reduced back to metal before further hydride experiments are possible.

Figure 1. Neutron diffraction pattern for the protactinium sample. The reflection markers for the three phases present are identified as follows: top - PaO, middle - Pa metal, and bottom - vanadium from the encapsulation.

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: R. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3317																									
Title: Structure Refinement of Synthetic Goethite (FeOOH)		Report received: <i>(for LANSCE use only)</i> 6/24/91																									
Authors and affiliations: Michael H. Ebinger, EES-15, LANL, MS J495 David L. Bish, EES-1, LANL, MS D469 Robert B. Von Dreele, LANSCE, MS H 805																											
Experiment report: <p>The original proposal was to examine FeOOD, however recent developments in intensity at LANSCE allowed us to perform the experiment on a small sample of FeOOH. A 2mm diameter quartz capillary with 256mg of FeOOH was examined on HIPD at 300K for 378.5μA-hr (5.4hr). Data from the $\pm 153^\circ$ banks was subsequently refined using GSAS (Larson & Von Dreele, 1990). To reduce the effects of the magnetic scattering the region of the pattern extending beyond a d-spacing of 3.0$\text{\AA}$ was excluded from the calculations (Fig. 1). The sample contained 30.6% (by wt.) hematite (Fe₂O₃) from the Rietveld analysis. The structure of FeOOH (Table 1) agrees quite well with previously published structures (Forsyth, Hedley & Johnson, 1968 and Busing & Levy, 1958 for α-AlOOH). In the present case the H atom was found quite easily from a difference Fourier (Fig. 2) phased with refined Fe and O atom positions.</p> <p>Table 1 Structure of Goethite</p> <p>Space group P b n m, a=4.602(5)$\text{\AA}$, b=9.958(11)$\text{\AA}$, c=3.018(3)$\text{\AA}$</p> <table border="1"> <thead> <tr> <th>Atom</th> <th>x</th> <th>y</th> <th>z</th> <th>U_{iso}, $\text{\AA}^2$</th> </tr> </thead> <tbody> <tr> <td>Fe</td> <td>-0.0508(8)</td> <td>0.1460(4)</td> <td>1/4</td> <td>0.0043(9)</td> </tr> <tr> <td>O(1)</td> <td>0.2953(15)</td> <td>-0.2008(6)</td> <td>1/4</td> <td>0.0024(10)</td> </tr> <tr> <td>O(2)</td> <td>-0.2009(16)</td> <td>-0.0517(6)</td> <td>1/4</td> <td>0.0033(11)</td> </tr> <tr> <td>H</td> <td>-0.394(4)</td> <td>-0.0801(16)</td> <td>1/4</td> <td></td> </tr> </tbody> </table> <p>U₁₁=0.044(10), U₂₂=0.021(7), U₃₃=0.040(7), U₁₂=0.008(6) $\text{\AA}^2$</p> <p>R_{wp}=2.41%, R_p=1.72% for $\pm 153^\circ$ detector bank data</p> <p>Goethite in this sample exhibits considerable crystallite and microstrain broadening while the hematite shows only microstrain broadening. The broadening for both goethite and hematite is also strongly anisotropic. For goethite the microstrain parallel to the (001) axis is 0.37%; the perpendicular component is 0.40%. The crystallites average 240$\text{\AA}$ along (001) and 230$\text{\AA}$ perpendicular to (001). For hematite the microstrain is much larger with 1.3% along (001) and 0.9% perpendicular to (001).</p>			Atom	x	y	z	U _{iso} , $\text{\AA}^2$	Fe	-0.0508(8)	0.1460(4)	1/4	0.0043(9)	O(1)	0.2953(15)	-0.2008(6)	1/4	0.0024(10)	O(2)	-0.2009(16)	-0.0517(6)	1/4	0.0033(11)	H	-0.394(4)	-0.0801(16)	1/4	
Atom	x	y	z	U _{iso} , $\text{\AA}^2$																							
Fe	-0.0508(8)	0.1460(4)	1/4	0.0043(9)																							
O(1)	0.2953(15)	-0.2008(6)	1/4	0.0024(10)																							
O(2)	-0.2009(16)	-0.0517(6)	1/4	0.0033(11)																							
H	-0.394(4)	-0.0801(16)	1/4																								

Experiment report (continued):

Figure 1. Observed and calculated profile intensities from the +153° bank. Lower row of reflection markers is for goethite, upper row is for hematite. Calculated background values have been subtracted from both observed and calculated intensities.

Figure 2. Difference Fourier section for goethite at $z=1/4$ phased with Fe and O atom positions. Depressions marked H correspond to hydrogen atom positions

References:

W.R. Busing & H.A. Levy (1958). Acta Crystallogr. 11, 798-803.

J.B. Forsyth, I.G. Headley & C.E. Johnson (1968). J. Phys. C, 179-188.

A.C. Larson & R.B. Von Dreele (1990). "GSAS - General Structure Analysis System", Los Alamos National Laboratory Report LAUR 86-748.

Instrument used: <i>(please type)</i> HIPD	Local contact: Dr. Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3319.1
Title: STRUCTURE OF $\text{Rb}_{24}\text{Be}_{24}\text{As}_{24}\text{O}_{96} \cdot n\text{H}_2\text{O}$: A NEW COMPOSITION FOR THE ZEOLITE RHO FRAMEWORK TOPOLOGY.		Report received: <i>(for LANSCE use only)</i> 10-9-90
Authors and affiliations: J. Parise, (Earth and Space Sciences, SUNY, Stony Brook, NY), R. Harlow, T. E. Gier, D. R. Corbin (Experimental Station, DuPont, Wilmington, DE) and R. Von Dreele (Los Alamos, NM)		
<p>Experiment report:</p> <p>Several compositions crystallizing with the structure of zeolite RHO have been synthesized. In the aluminosilicate system, this structure type has the largest known changes in unit cell dimension upon dehydration and loading. We are carrying out systematic structural investigations as a function of temperature and extra-framework cation composition¹ in order to better understand the factors affecting the distortion of the framework. This task is aided by the ability to synthesize new compositions for the framework of RHO and to compare the flexibility of these new structures with that of the aluminosilicates containing the same extra-framework cations. We have refined the structure of $\text{Rb}_{24}\text{Be}_{24}\text{As}_{24}\text{O}_{96}$ (I23, $a = 14.001(1)\text{\AA}$) using a combination of x-ray data collected at X-7A, neutron data obtained at the LANSCE HIPD, Los Alamos, and soft constraints, based upon the data obtained by Corbin <i>et al.</i>¹ on the Be-P analogue, the mineral pahasapaite (nominally $\text{Ca}_6\text{LiBe}_{24}\text{P}_{24}\text{O}_{24}$). Table 1 lists the atomic parameters and occupancies of the extra framework sites along with the discrepancy factors for the two powder data sets². The structure is similar to that reported by Harlow <i>et al.</i> (in press) for the dehydrated pahasapaite. However, in the arsenate the smaller Be^{2+} resides on the site occupied by P^{5+} in the structure of pahasapaite. This accords with the relative ionic sizes $r_{\text{As}^{5+}} = 0.335\text{\AA}$, $r_{\text{P}^{5+}} = 0.17\text{\AA}$ and $r_{\text{Be}^{2+}} = 0.27\text{\AA}$.</p>		

Experiment report (continued):

TABLE 1. Final refined atomic parameters for $\text{Rb}_{24}\text{Be}_{24}\text{As}_{24}\text{O}_{96}$. Common thermal parameters for the framework (Be, As, O) and extra-framework atoms (Rb and H_2O) were refined to values of $U \times 10^2 (\text{\AA}^2) = 2.0(1)$ and $4.6(2)$, respectively. For the x-ray data: $R_{\text{wp}} = 0.056$, $R_N = 0.054$; for the neutron data: $R_{\text{wp}} = 0.128$, $R_N = 0.093$; combined $\chi^2 = 3.8$

ATOM	X	Y	Z	occ.
Be(1)	0.2719(3)	0.1264(3)	0.4298(2)	1
O(1)	0.2342(2)	0.2337(3)	0.3964(2)	1
O(2)	0.3825(3)	0.1282(2)	0.3881(3)	1
O(3)	0.2980(4)	0.1151(3)	0.5440(2)	1
O(4)	0.2166(4)	0.0460(2)	0.3652(4)	1
As(1)	0.2230(3)	0.9264(3)	0.3741(3)	1
Rb(1)	0.5	0.5	0	1
Rb(2)	0.1887(3)	0.1887(3)	0.1887(3)	0.875
Rb(3)	0.3752(4)	0.3752(4)	0.3752(4)	0.700
Rb(4)	0.314(1)	0.314(1)	0.314(1)	0.300
Rb(5)	0.263(1)	0	0	0.250
H2O(1)	0.0660(5)	0.0660(5)	0.0660(5)	0.615(9)
H2O(2)	0.4507(6)	0.4507(6)	0.4507(6)	0.319(9)

References:

1. D. R. Corbin *et al.*, J. Am. Chem Soc., in press
2. A. C. Larson and R. B. Von Dreele, GSAS manual, LAUR report 86748.

Instrument used: <i>(please type)</i> HIPD	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 3334
Title: The molecular orientation of bilayer phospholipids.		Report received: <i>(for LANSCE use only)</i> 2/28/91
Authors and affiliations: Gregory S. Smith, LANSCE William Hamilton, LANSCE		
Experiment report: <p>Previously, the in-plane structure of DMPC-water systems have been studied using x-ray scattering[1,2]. We have extended this work to a preliminary study of the relationship of the glycerol backbone to the position of the tails in the hexagonal in-plane lattice of the LβF phase of a phospholipid-water system. 3.0 grams of dimyristoyl phosphotidyl choline (DMPC) were obtained from Avanti Polar Lipids in which the fatty acid chain in the second position had been fully deuterated. If there is a structure associated with the backbone orientation[3], there is a deviation from the scattering one would expect for an in-plane hexagonal lattice.</p> <p>Two sets of samples were prepared. The first set used partially deuterated DMPC plus H₂O and the other used protonated DMPC plus D₂O. The samples were prepared by mixing the water with the DMPC to obtain a 25% D₂O by weight mixture. This put the sample in the LβF phase at room temperature. The plots of intensity versus d-spacing are shown in figures 1 and 2 for the 90 and 5 degree detector banks. As expected, the layer repeat spacing is about 45 Å for the deuterated samples and 25 Å (weak peak) for the protonated samples in H₂O. This is because the hydrocarbon chains have nearly the same scattering length as the water and the unit cell can be defined as half of a bilayer. The important region of interest is where we expect the data for the in-plane structure. In both cases,</p>		

Experiment report (continued):

we don't see any peaks in this region. It is unclear why this is the case since we had previously observed in-plane structure for this system with approximately the same volume of sample. We feel that the resolution and signal to noise afforded by this instrument is not sufficient to solve this problem.

Figure 1

Figure 2

References:

- (1) G. S. Smith, C. R. Safinya, D. Roux, and N. A. Clark, *Mol. Cryst. Liq. Cryst.*, **144**, 235(1987).
- (2) G. S. Smith, E. B. Sirota, C. R. Safinya, and N. A. Clark, *Phys. Rev. Lett.*, **60**, 813(1988).
- (3) I. Hatta, S. Kato, K. Ohki, and K. Tsuchida, *Mol. Cryst. Liq. Cryst.*, **139**, (1986).

Instrument used: <i>(please type)</i> HIPD	Local contact: Robert B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3325.1
Title: Neutron powder diffraction studies on some strongly oxidizing transition metal fluorides		Report received: <i>(for LANSCE use only)</i> 3.1/91
Authors and affiliations: Boris Žemva, Karel Lutar and Adolf Jesih "Jožef Stefan" Institute, University of Ljubljana, 61000 Ljubljana, Slovenia William J. Casteel, Jr., Rika Hagiwara, Horst Borrmann and Neil Bartlett Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720 Angus P. Wilkinson Department of Chemical Crystallography, The University of Oxford, England, OX1 3PD David E. Cox The Department of Physics, Brookhaven National Laboratory, Upton, Long Island, N.Y. 11973 Robert B. Von Dreele Manuel Lujan, Jr., Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, N.M. 87545		
Experiment report: 1) NEW TETRAFLUORIDE STRUCTURES AND A NEW STRUCTURE TYPE REPRESENTED BY RuF_4 . <p>Recently a general route to binary transition metal fluorides has been found which provides high purity tetrafluorides or trifluorides. This has provided ReF_4, OsF_4, and RuF_4, which have been structurally characterized. X-ray powder data for ReF_4 and OsF_4 have been indexed on the basis of orthorhombic unit cells (probable space group Fdd2) and appear to be structurally similar to RhF_4, IrF_4, PtF_4, and PdF_4. This structure is based on that of rutile with half of the metal atoms missing and in which the metal atom is octahedrally coordinated to four F, shared equally with four other metal atoms, and two <u>cis</u> unshared F ligands. The structure of RuF_4 is of a new type. The monoclinic unit cell (space group $\text{P } 2_1/n$) has $a=5.611$, $b=4.950$, $c=5.411 \text{ \AA}$, $\beta=121.36^\circ$ with metal atoms at 000 and $1/2 \ 1/2 \ 1/2$. Each Ru atom is octahedrally coordinated with F ligands, the two unshared F being trans to one another. The four shared F ligands are in a bent Ru - F - Ru arrangement, the angle being 136°. The structure of RuF_4 is thus a puckered sheet version of the NbF_4 planar sheet structure, in which the shared Nb - F - Nb set is linear.</p> <p>This paper was presented at the "ACS Tenth Winter Fluorine Conference" in St. Petersburg, Florida, 1991.</p>		

Experiment report (*continued*):

- 2) For the mixed-valence silverfluoride Ag_2F_8 we have not yet been able to index the powder pattern, while the compound Ag_3F_8 so far lacks proper crystallinity.
- 3) AgAsF_6 is obviously disordered at room temperature and therefore a temperature dependent study is under its way.
- 4) For CrF_4 the crystallinity of the samples needs to be improved before a solution of the structure will be possible.

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: Robert B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3335.2
Title: Silver Trifluoride: Preparation, Crystal Structure, Some Properties and Comparison with AuF ₃		Report received: <i>(for LANSCE use only)</i> 3/1/91
Authors and affiliations: Boris Žemva, Karel Lutar and Adolf Jesih "Jožef Stefan" Institute, University of Ljubljana, 61000 Ljubljana, Slovenia William J. Casteel, Jr., Horst Borrmann and Neil Bartlett Chemical Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720 Angus P. Wilkinson Department of Chemical Crystallography, The University of Oxford, England, OX1 3PD David E. Cox The Department of Physics, Brookhaven National Laboratory, Upton, Long Island, N.Y. 11973 Robert B. Von Dreele Manuel Lujan, Jr., Neutron Scattering Center, Los Alamos National Laboratory, Los Alamos, N.M. 87545		
Experiment report: <p><u>Abstract:</u> Red, diamagnetic AgF₃ is precipitated from anhydrous hydrogen fluoride (AHF) solutions of AgF₄⁻ salts by addition of fluoroacids (L) such as BF₃, PF₅ or AsF₅: AgF₄⁻ + L → AgF₃ + LF⁻. With additional AsF₅, silver(III) is reduced: AgF₃ + AsF₅ → AgFAsF₆ + 1/2F₂ but such reduction does not occur with BF₃ and the latter acid is therefore preferred for the preparation of stoichiometric AgF₃. AgF₃ is thermodynamically unstable and, in contact with AHF, at ~ 20°C, loses F₂ in less than 19 hrs. according to the equation: 3AgF₃ → Ag₃F₈ + 1/2F₂. The trifluoride is isostructural with AuF₃. To provide for meaningful comparisons the structure of AuF₃ was redetermined. The structures of both AgF₃ and AuF₃ were successfully refined in space group P6₃22 - D₆₂ (No. 178) using the Rietveld method with time-of-flight neutron powder diffraction data from 100mg samples contained in 2mm capillary tubes. The 7762 observations for AgF₃ yielded a = 5.0782(2), c = 15.4524(8) Å, V = 345.10(2) Å³, the reliability parameters for the structure being R_{wp} = 6.21 and R_p = 3.83%. From the 7646 observations for AuF₃, a = 5.1508(1), c = 16.2637(7) Å, V = 373.68(2) Å³ and R_{wp} = 11.21 and R_p = 7.58%. The silver or gold atom lies at the center of an elongated octahedron with two Ag-F(1) = 1.990(3), two Au-F(1) = 1.998(2); two Ag-F(2) = 1.863(4); two Au-F(2) = 1.868(3) Å, the approximately square, isodimensional AF₄ units being joined by symmetrical μ-fluorobridges (two F(1) in <u>cis</u> relationship in the AF₄ unit) to form the 6₁ (or 6₅) helical chains, the angle Ag-F(1)-Ag being 123.2(2)° and the Au-F(1)-Au being 119.3(2)°. The ~ 5 Å³ smaller formula unit volume of AgF₃ compared with AuF₃ and the shorter <u>z</u> axis interatomic distance (Ag-F = 2.540(4), Au-F = 2.756(8) Å) is in accord with the tighter binding of the Ag(III) <u>d</u> orbital electrons evident in the strong oxidizing properties of Ag(III). Interaction of AgF⁺ with AgF₄⁻ (1:1) in AHF yields maroon Ag(II)Ag(III)F₅. The</p>		

Experiment report (continued):

latter interacts with AgF_3 to yield $\text{Ag(II)Ag(III)}_2\text{F}_8$, which is identical to the product of the decomposition of AgF_3 at 20°C in AHF and with the material previously described^{1,2} as AgF_3 . The magnetic susceptibility for $\text{Ag(II)Ag(III)}_2\text{F}_8$ obeys the Curie-Weiss law (4 to 280K) with $\theta = -4.2(5)^\circ$ and $\mu_{\text{eff}} = 1.924(3)$ B.M.

Portion of the fitted neutron time-of-flight powder diffraction pattern for data taken on the $+153^\circ$ 2 θ bank for AgF_3 . The observed values are shown as (+) and the calculated values from the best fit are shown as a curve. A difference ($I_{\text{obs}} - I_{\text{calc}}$) curve and the reflection positions are also shown. All intensity values are normalized by a previously measured incident spectrum.

References:

Accepted for publication in J. Amer. Chem. Soc. (1991)

Instrument used: <i>(please type)</i> HIPD	Local contact: A. C. Lawson	Proposal number: <i>(for LANSCE use only)</i> 3341.0
Title: NEUTRON POWDER DIFFRACTION STUDY of MAGNETIC ORDER IN α -MANGANESE METAL		Report received: <i>(for LANSCE use only)</i> 1/18/91
Authors and affiliations: A. C. Lawson, MST-5 Z. Fisk, CMS Los Alamos National Laboratory Los Alamos NM 87545 M. Aronson, Department of Physics University of Michigan Ann Arbor MI 48109		
<p>We used the High Intensity Powder Diffractometer (HIPD) to study the development of magnetic order in α-manganese metal. α-Mn has a body-centered cubic structure with 58 atoms per unit cell and a correspondingly complicated magnetic structure. The original purpose of the experiment was to study the magnetic behavior in the vicinity of 25 K, where measurement of transport properties and susceptibility - especially under pressure - had shown some anomalies. We used about four days of beam time to collect data at 14 temperatures between 15 and 305 K.</p> <p>Lattice constants versus temperature are shown in Fig. 1. There is a distinct thermal expansion anomaly at 105 K, the accepted Néel temperature of α-Mn. Below the Néel temperature, only anti-body-centered magnetic reflections were observed. Fig. 2 shows the magnetic intensities of 5 magnetic reflections plotted versus temperature.</p> <p>We observed a distinct splitting of the (111) magnetic reflection. The splitting was not completely resolved in the 40° bank but was unambiguous (albeit with rather poor statistics) in the 90° bank. The fitted intensities from the 40° bank are shown in Fig. 3, and the observed d-spacings are shown in Fig. 4. Splitting of the (111) magnetic reflection was also observed in a neutron single crystal study but was attributed to "subgrain structure" effects. [T. Yamada et al., J. Phys. Soc. Japan <u>28</u> 615 (1970)] This explanation will not work for a powder sample.</p> <p>We did not observe any clear anomalies near 25 K. This is not too surprising, as the low temperature anomalies are most clearly observed under pressure. The observation of the satellite peak in a powder sample is quite interesting, as it indicates that the magnetic structure of α-manganese is even more complicated than previously supposed.</p> <p>We wish to thank Andrew Cheng for his contributions to the data analysis and Roger Pynn for his comments on the interpretation of the satellite peak.</p>		

Experiment report (continued):

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3360
Title: Extinction and Absorption in Polycrystalline Materials		Report received: <i>(for LANSCE use only)</i> 6/24/91

Authors and affiliations:

T.M. Sabine, Dept. of Physics, University of Technology, Sydney, Australia
W. Kalceff, Dept. of Physics, University of Technology, Sydney, Australia
R.B. Von Dreele, LANSCE, MS H805, Los Alamos National Laboratory

Experiment report:

The object of the proposed experiment was to examine the effects of absorption on the primary extinction in the observed diffraction intensities from a large grained powder sample. A ~50mg sample of 20%Gd doped <20 μ m particle size CeO₂ (kindly provided by J. Cline of NIST) contained in a 1mm diameter quartz capillary was examined twice on HIPD. For the first attempt, the capillary tube was placed inside a standard 3/8" vanadium can; no scattering from the sample was observed in a ~2hr run. In fact only the very weak Bragg peaks from the vanadium were seen in the pattern. For a second attempt, the capillary was suspended in the neutron beam and examined for 2.62hr (184 μ A-hr). Despite the fact that the background was considerably lower, Bragg scattering from the sample was essentially not seen (Fig. 1) except at the lower scattering angles ($\pm 40^\circ$). A calculation based on the neutron absorption expected from the 20%Gd suggested that the effective sample size for backscattering was ~1mg. At lower scattering angles the Bragg peaks are observed with shorter wavelength neutrons and hence the absorption is less. No analysis of this data was attempted.

Experiment report (continued):

Figure 1. Powder diffraction patterns from 50mg sample of 20%Gd doped CeO_2 . Data is normalized by monitor counts and covers $1.0 \leq d \leq 2.0 \text{ \AA}$ for $+153^\circ$, -90° and $+40^\circ$ banks of HIPD.

References:

Instrument used: (please type) HIPD	Local contact: Robert Von Deelee	Proposal number: <i>(for LANSCE use only)</i> 3363
Title: Structures of the Two Solid Phases of the Chlorofluorocarbon CHClF_2		Report received: <i>(for LANSCE use only)</i> 1/25/91
Authors and affiliations: Bruce Torrie and Abarrul Ikram, Department of Physics, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1 Robert Von Dreele, LANSCE, Los Alamos National Laboratory		
Experiment report: <p>A number of the halogen derivatives of methane have been examined in the solid state using Raman and infrared techniques to study the dynamics of the molecules and neutron powder profile techniques to determine the structures. Previous efforts were described in a review article [1] and in a series of articles of which the most recent ones deal with chloriodomethane [2] and methylene bromide and methylene iodide [3]. Attempts have also been made to simulate structures and dynamics using intermolecular potentials [4].</p> <p>Interest in CHClF_2 was stimulated by a recent Raman and infrared study in our laboratory. An unexpected result of the experiments was the discovery of a phase transition between liquid nitrogen and liquid helium temperatures. Most transitions in molecular crystals occur at higher temperatures.</p> <p>The figures show the powder profiles of CHClF_2 at 50K and 10K. A detailed analysis has only begun but it is clear that there is a phase transition between the two temperatures and it seems likely that there is a doubling in the volume of the unit cell on going to the lower temperature.</p>		

Experiment report (continued):

FREON-22 AGAIN AT 10 K

BANK NO. = 3 TWO-THETA = 90.00 OBSERVED PROFILE

21 OCT 90 14 40 43

FREON-22 AT 50 K

BANK NO. = 3 TWO-THETA = 90.00 OBSERVED PROFILE

21 DEC 90 14 37 35

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1. A. Anderson, B. Andrews and B.H. Torrie, J. de Chim. Phys. 82, 99 (1985).
2. B.H. Torrie, D.A. Prystupa, J. Clark, S. Taylor and Y.W. Wang, J. Raman Spectrosc. 21, 423 (1990).
3. D.A. Prystupa and B.H. Torrie, B.M. Powell and P.N. Gerlach, Molec. Phys. 68, 835 (1989).
4. B.H. Torrie and B.M. Powell, J. Phys. Condens. Matter 1, 5827 (1989).

Instrument used: <i>(please type)</i> H.I.P.D.	Local contact: Robert B. VonDreele	Proposal number: <i>(for LANSCE use only)</i> 3378				
Title: STRUCTURE OF POTASSIUM SILICATES		Report received: <i>(for LANSCE use only)</i> 2/27/91				
Authors and affiliations: <table border="0"> <tr> <td>B.J. Olivier and D.W. Schaefer Sandia National Laboratories Division 1810 Albuquerque, NM 87185-5800</td> <td>R.B. VonDreele L.A.N.S.C.E. Los Alamos National Laboratories Los Alamos, NM 87545</td> </tr> <tr> <td>Steve Martin Materials Science Department Iowa State University Ames, IA 50011</td> <td>K.D. Keefer Materials Science Department University of Cincinnati Cincinnati, OH 45221</td> </tr> </table>			B.J. Olivier and D.W. Schaefer Sandia National Laboratories Division 1810 Albuquerque, NM 87185-5800	R.B. VonDreele L.A.N.S.C.E. Los Alamos National Laboratories Los Alamos, NM 87545	Steve Martin Materials Science Department Iowa State University Ames, IA 50011	K.D. Keefer Materials Science Department University of Cincinnati Cincinnati, OH 45221
B.J. Olivier and D.W. Schaefer Sandia National Laboratories Division 1810 Albuquerque, NM 87185-5800	R.B. VonDreele L.A.N.S.C.E. Los Alamos National Laboratories Los Alamos, NM 87545					
Steve Martin Materials Science Department Iowa State University Ames, IA 50011	K.D. Keefer Materials Science Department University of Cincinnati Cincinnati, OH 45221					
Experiment report: <p>The recent introduction of the fracton excitation¹ and the elusive understanding of the glass transition² has left the glassy state of matter a topic of interest for decades. Continuous improvements to neutron flux and energy resolutions of neutron spectrometers have led to more insightful understandings of the structural and topological arrangements of this exciting state. Unfortunately, a consistent description relating the glass transition to the network connectivity and low energy dynamics is lacking. Therefore, we propose a systematic study relating the atomic positioning with network connectivity and low energy excitations would be of interest.</p> <p>A strong candidate for such a systematic would be the multi-component silicate glass, $(K_2O)_x(SiO_2)_{1-x}$. For small coordination numbers, below the rigidity threshold, potassium silicate is expected to be soft³ and the dynamics are supposed to be dominated by low energy phonons. Conversely, if the network is fractal, the excitations expected would be fractons. One obviously expects this so called " floppy mode " regime to be intimately related to the positioning of the potassium ions.</p>						

Experiment report (continued):

It is our aim in this study to determine the relative positioning of the K^+ ions with respect to the Si and O atoms, i.e., whether or not the intercalation of the potassium ions was random. An earlier study⁴ suggests the substitution of sodium or lithium into SiO_2 is not random. The figure below shows preliminary diffraction patterns for amorphous SiO_2 and $(K_2O)_x(SiO_2)_{1-x}$ where $x=0.3$ and 0.5 respectively. The data represent the bank of detectors positioned at $2\theta=14^\circ$. No corrections have yet been made for incident spectra, adsorption, self-shielding, and inelastic events. The Fourier transform (RDF) of the corrected data should give the respective coordination numbers. This study will compliment recent inelastic measurements previously taken at NIST.

Fig. 1 The diffraction patterns for the above named silicates. The data has not been corrected for the incident spectrum.

References:

- 1.) S.Alexander and R.Orbach, J. Phys. Lett. **43**, L625 (1982).
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- 3.) Y.Cai and M.F.Thorpe, Phys. Rev. B, **40**, 535, (1989).
- 4.) M.Misawa, D.L.Price, and K.Suzuki, J. Non-Cryst. Solids, **37**, 85, (1987).

Instrument used: (please type) Neutron Powder Diffractometer	Local contact: Dr. Robert Von Dreele	Proposal number: (for LANSCE use only) 3384.1)
A study of Al/Si order at the high-low leucite phase transition using high-temperature powder neutron diffraction and Rietveld refinement		Report received: (for LANSCE use only) 3/21/91
<p>Peter J. Heaney and Jeffrey E. Post Dept. Mineral Sciences NHB 119 Smithsonian Inst. Washington, D.C. 20560</p> <p>Early X-ray diffraction studies of the mineral leucite (KAlSi_2O_6) indicated that leucite transforms displacively at 650°C from a structure with space group $I4_1/a$ to one with space group $Ia\bar{3}d$ (Wyart, 1938; Sadanaga and Ozawa, 1968; Peacor, 1968). However, calorimetric experiments by Faust (1963) and Lange et al. (1986) have discerned two absorption events near the leucite transition separated by ~25°C. Based on this evidence, many researchers (Grögel et al., 1984; Lange et al., 1986; Rüscher et al., 1987) have proposed that leucite passes through an intermediate phase with space group $I4_1/acd$ as it transforms from the low to the high temperature polymorph.</p> <p>In order to reconcile results obtained from X-ray diffraction with calorimetric data, Heaney and Veblen (1990) performed <i>in situ</i> heating experiments on leucite with the transmission electron microscope. Their observations based on electron diffraction were consistent with X-ray diffraction experiments, but dark-field images of the twins of leucite at high temperature revealed that above T_c the structure is not rigorously cubic. Thus, these TEM experiments could not explain the two thermal events associated with the transition, and they raised questions regarding the failure of leucite to transform "completely" at high temperature.</p> <p>A possible cause of some of the anomalies observed at the leucite transition may be Al/Si order among the tetrahedral sites. Such order is forbidden in the $Ia\bar{3}d$ space group, and X-ray experiments have failed to detect evidence of order in either the</p>		

high or the low temperature polymorphs. On the other hand, two MAS/NMR experiments using ^{29}Si have detected short range order among the three tetrahedral sites of low leucite (Brown et al., 1987; Murdoch et al., 1988).

Because the neutron scattering factors for Al and Si are somewhat different, it was thought that Rietveld refinement of neutron diffraction data might reveal preferential partitioning of Al and Si into the tetrahedral sites. Moreover, structure refinements of leucite at several temperatures surrounding the transition might indicate the cause of the two absorption events observed by calorimetry. Accordingly, powdered leucite from Napoli, Italy (USNM #167389) first was analyzed by differential scanning calorimetry to determine the temperatures of the two absorption events (635°C and 655°C). Twelve neutron diffraction experiments then were performed at the following temperatures (°C): 23; 300; 500; 600; 610; 620; 630; 636; 642; 646; 652; 665. Rietveld refinement of these data using the GSAS program of Larson and Von Dreele is in progress. Preliminary results indicate no Al/Si order among the tetrahedral sites of leucite at any of the observed temperatures can be demonstrated convincingly, suggesting that if order is present it must occur over short ranges.

- Brown, I.W.M., Cardile, C.M., MacKenzie, K.J.D., Ryan, M.J., and Meinhold, R.H. (1987) Natural and synthetic leucites studied by solid state ^{29}Si and ^{27}Al NMR and ^{57}Fe Mossbauer spectroscopy. *Physics and Chemistry of Minerals*, 15, 78-83.
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Instrument used: <i>(please type)</i> Neutron Powder Diffractometer	Local contact: Dr. Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3385.0
Title: Determination of hydrogen positions in fine-grained silica varieties by powder neutron diffraction and Rietveld refinement		Report received: <i>(for LANSCE use only)</i> 3/21/91
Authors and affiliations: Peter J. Heaney and Jeffrey E. Post Dept. Mineral Sciences NHB 119 Smithsonian Institution Washington, D.C. 20560		
Experiment report: <p>A significant fraction of the quartz contained within the earth's crust occurs in microcrystalline form; chalcedony and chert are common in igneous, metamorphic, and sedimentary rocks alike. Early powder X-ray diffraction studies of microgranular quartz species revealed no differences between chalcedony and prismatic low quartz, and microcrystalline silica varieties conventionally have been considered structurally identical to coarse-grained quartz. However, recent work by Flörke et al. (1982) and by Graetsch et al. (1987) has emphasized the significance of a compositional disparity between chalcedony and quartz -- namely, the inclusion of approximately 2 wt.% H₂O in chalcedony. Infra-red spectroscopy by Flörke et al. (1982) suggests that this water is divided more or less equally between molecular H₂O and silanole-group water (SiOH), and by the same method Graetsch et al. (1987) conclude that two-thirds of the silanole-group water is located along structural defects. These results suggest that 0.3 wt.% H₂O may be incorporated into quartz as structural hydroxyl.</p> <p>The inclusion of water in quartz can greatly affect its macroscopic qualities, particularly in terms of hydrolytic weakening, but the position of hydrogen within the structure of quartz has not been clarified by diffraction methods. Electron diffraction of the chalcedony in agates by transmission electron microscopy reveals superperiodicities of 3, 4, and 5 times the primary translations in quartz (Heaney and Veblen, 1988).</p>		

In addition, powder X-ray diffraction patterns of chalcedonies and cherts reveal a minor peak corresponding to the the (001) planes of quartz (Heaney and Post, unpub.); this peak violates the $P3_121$ symmetry of low quartz. Both of these anomalies in the diffraction behavior of microcrystalline quartz may arise from minor distortions of the crystal structure due to the incorporation of hydrogen.

As neutron diffraction is a sensitive indicator of hydrogen atom positions in crystal structures, neutron powder diffraction patterns were collected from a specimen of silicified coral from the Hillsborough Bay formation, Florida (USNM #47899). Wet chemical analysis indicated that this material contained 0.17 wt.% adsorbed H_2O and 1.91 wt.% structural H_2O . Separate neutron experiments were performed on untreated samples, deuterated samples, and samples dried at $110^\circ C$ for 1 hr. Results from the three samples were not significantly different.

Neutron powder diffraction patterns manifested no peaks indicative of a superlattice and no violations of the three-fold screw symmetry. Since reflections corresponding to (001) of quartz had been observed for this material using X-rays, we suspect that this peak is absent because of low structure factor intensity. Rietveld refinement of the structure was performed using the GSAS program of Larson and Von Dreele. The data for ideal low quartz of Wright and Lehmann (1981) supplied the starting parameters, and difference Fourier maps were calculated in an attempt to discern regions of anomalously high intensity that might correspond to structural hydrogen. However, no intensity above background was observed, perhaps indicating that hydrogen positions are disordered over large length scales. Therefore, the location of hydrogen in fine-grained quartz remains unresolved.

References:

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- Wright, A.F. and Lehmann, M.S. (1981) The structure of quartz at 25 and $590^\circ C$ determined by neutron diffraction. *Journal of Solid State Chemistry*, 36, 371-380.

Instrument used: <i>(please type)</i> High-Intensity Powder Diffractometer (HIPD)	Local contact: Dr. Bob Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3408.0
Title: Low-Temperature Studies of Rubidium and Cesium Deuteride		Report received: <i>(for LANSCE use only)</i> 1/2/91
Authors and affiliations: Nathaniel E. Brese and Michael O'Keeffe Department of Chemistry Arizona State University Tempe, AZ 85287-1604		
Experiment report: <p>RbD and CsD were studied by X-ray diffraction in 1931. Only the face-centered arrangement of the metal atoms could be determined, so the B1 (rocksalt) and B3 (sphalerite) structures were equally likely. These structures are easily discernible using neutron diffraction; for example, the intensity of the (200) reflection is calculated to be 0 and 100 for RbD with the rocksalt and sphalerite structures, respectively.</p> <p>A minimum of data were collected; noisy data resulted in high residuals, but RbD and CsD were shown unambiguously to have the B1 (rocksalt) structure. Rubidium deuteride, RbD: $M_r = 87.47$, cubic, $Fm\bar{3}m$, $a = 5.9705(2) \text{ \AA}$ (10K), $a = 6.0210(2) \text{ \AA}$ (300K), $V = 212.83(2) \text{ \AA}^3$ (10K), $V = 218.27(2) \text{ \AA}^3$ (300K), $Z = 4$, $D_x = 2.66 \text{ g cm}^{-3}$ (300K), Rietveld refinement (GSAS), wR_p, R_p, reduced χ^2 are 0.045, 0.031, 3.99 (10K), respectively, and 0.052, 0.037, 2.19 (300K), respectively. Cesium deuteride, CsD: $M_r = 134.92$, cubic, $Fm\bar{3}m$, $a = 6.3741(3) \text{ \AA}$, $V = 258.97(4) \text{ \AA}^3$, $Z = 4$, $D_x = 3.46 \text{ g cm}^{-3}$, 300K, Rietveld refinement (GSAS), wR_p, R_p, and reduced χ^2 are 0.070, 0.048, 1.30, respectively.</p> <p>This work has been accepted by Acta Crystallographica as a short-format paper in section C.</p>		

Experiment report (continued):

RbD, 10K

RbD, 300K

CsD, 300K

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: Dr. Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 100006																																																
Title: Lattice Parameter Variations in Deuterated Palladium Lithium Alloys of Varing Compositions.		Report received: <i>(for LANSCE use only)</i> 3/1/91																																																
Authors and affiliations: Carol L. Talcott MST-3 Edmund K. Storms NMT-1 Andrew Lawson MST-5 Mary Ann David MST-3																																																		
Experiment report: <p>A neutron diffraction study of six palladium lithium deuteride samples (PdLi_xD_y) was done using the High Intensity Powder Diffractometer (HIPD) at LANSCE. The experiment showed a decreasing lattice constant as a function of increaseing lithium content in the alloy for both the alpha and beta phases.</p> <p>Each sample was arc-melted in an Argon atmosphere and loaded with deuterium in an electrolytic cell. The samples were loaded well into the beta phase ($\text{D/M} > 0.6$) and then deuterium gas was desorbed from the sample in an oven at 175 C until the sample was approximately half beta ($\text{D/M} = 0.6$) and half alpha ($\text{D/M} = 0.03$). The hydride was then sealed in a vanadium sample container with a small piece of copper wire inserted as a standard. The sample was kept at 300 K with a small overpressure of deuterium (approximately 25 torr).</p> <p>Table 1 and figure 1 show the results from this work. The beta phase shows a sharp decline in lattice constant as the lithium content in the sample increases. The alpha material shows a smaller drop, but still significant. We were unable to determine the position of lithium in the palladium lattice unambiguously.</p> <p style="text-align: center;">TABLE 1</p> <table border="1"> <thead> <tr> <th>% Li[#] (Atomic)</th> <th colspan="2">Beta lattice / corrected[*] (Angstroms)</th> <th colspan="2">Alpha lattice / corrected[*] (Angstroms)</th> <th>Cu lattice (Angstroms)</th> </tr> </thead> <tbody> <tr> <td>0.0000</td> <td>3.9922 / 3.99038</td> <td>+/-0.0002</td> <td>3.8885 / 3.88673</td> <td>+/-0.0002</td> <td>3.6164</td> </tr> <tr> <td>0.0012</td> <td>3.9944 / 3.99269</td> <td>+/-0.0002</td> <td>3.8893 / 3.88763</td> <td>+/-0.0002</td> <td>3.6163</td> </tr> <tr> <td>0.02</td> <td>3.9989 / 3.99829</td> <td>+/-0.0002</td> <td>3.8917 / 3.89111</td> <td>+/-0.0002</td> <td>3.6153</td> </tr> <tr> <td>0.05</td> <td>4.0089 / 4.01173</td> <td>+/-0.0002</td> <td>3.8893 / 3.89205</td> <td>+/-0.0002</td> <td>3.6122</td> </tr> <tr> <td>0.07</td> <td>4.0180 / 4.01906</td> <td>+/-0.0002</td> <td>3.8927 / 3.89372</td> <td>+/-0.0002</td> <td>3.6138</td> </tr> <tr> <td>0.08</td> <td>4.0199 / 4.02018</td> <td>+/-0.0002</td> <td>3.8927 / 3.89297</td> <td>+/-0.0002</td> <td>3.6145</td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td></td> <td>(3.61475)</td> </tr> </tbody> </table> <p>[#]These are production estimates. All samples are being analyzed at the Analytical Chemistry Group at Los Alamos National Laboratory.</p> <p>[*]Corrected to Cu average.</p>			% Li [#] (Atomic)	Beta lattice / corrected [*] (Angstroms)		Alpha lattice / corrected [*] (Angstroms)		Cu lattice (Angstroms)	0.0000	3.9922 / 3.99038	+/-0.0002	3.8885 / 3.88673	+/-0.0002	3.6164	0.0012	3.9944 / 3.99269	+/-0.0002	3.8893 / 3.88763	+/-0.0002	3.6163	0.02	3.9989 / 3.99829	+/-0.0002	3.8917 / 3.89111	+/-0.0002	3.6153	0.05	4.0089 / 4.01173	+/-0.0002	3.8893 / 3.89205	+/-0.0002	3.6122	0.07	4.0180 / 4.01906	+/-0.0002	3.8927 / 3.89372	+/-0.0002	3.6138	0.08	4.0199 / 4.02018	+/-0.0002	3.8927 / 3.89297	+/-0.0002	3.6145						(3.61475)
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Experiment report (continued):

Lattice Constant vs. Lithium Content
in the Alpha and Beta Phases

Figure 1. Lattice constants of deuterided forms of palladium-lithium alloys. Alpha lattice constants are read on the right hand scale. Beta lattice constants are read on the left hand side.

References:

Instrument used: (please type) HIPD	Local contact: A. C. Lawson	Proposal number: (for LANSCE use only) 100016																									
Title: DEBYE-WALLER FACTORS of PdD _x MATERIALS		Report received: (for LANSCE use only) 12-7-90																									
Authors and affiliations: A. C. Lawson, MST- 5 J. W. Conant and V. A. Young, WX-5 Los Alamos National Laboratory Los Alamos NM 87545																											
<p>We have made a neutron diffraction study of some PdD_x materials on the High Intensity Powder Diffractometer (HIPD) at LANSCE. The four materials were pure Pd metal, α-PdD_x, and two samples of β-PdD_{0.6}. Of the two β samples, the one designated "Metz" was prepared from palladium black of very fine particle size. The deuterated samples were measured in sealed vanadium sample holders designed to hold the required pressure of deuterium gas at room temperature. Each sample (except Metz β) was measured at seven temperatures between 15 and 305 K. Lattice constants, deuterium fractions, microstrains and Debye-Waller factors were determined at each temperature by Rietveld refinement using GSAS.</p> <p>The lattice constants are shown in Figs. 1 and 2. The thermal expansion coefficients of the two beta samples are in good agreement except near room temperature. (The 300 K data for β-PdD_{0.6} were not taken in sequence with the other temperatures for this sample.) The overall discrepancy in lattice constants is associated with different deuterium fractions for the two β samples. The lattice constants for Pd metal and α-PdD_x are nearly identical; however, the curves cross one another at 200 K. We do not know the origin of this effect, but speculate that α-PdD_x may disproportionate below 200 K. Further work on this point is required.</p> <p>Debye-Waller curves are shown in Figs. 3 and 4. The Debye temperatures (θ) derived from these data are shown in the Table. The agreement between the values for the two β samples is especially gratifying in view of their different particle sizes (D).</p> <table border="1"> <thead> <tr> <th>sample</th> <th>θ [Pd] (K)</th> <th>θ [D] (K)</th> <th>Strain (%)</th> <th>D (Å)</th> </tr> </thead> <tbody> <tr> <td>Pd metal</td> <td>324(2)</td> <td>-</td> <td>0.57(1)</td> <td>-</td> </tr> <tr> <td>α-PdD_x</td> <td>329(3)</td> <td>-</td> <td>0.48(1)</td> <td>-</td> </tr> <tr> <td>β-PdD_x</td> <td>302(2)</td> <td>849(5)</td> <td>0.75(2)</td> <td>-</td> </tr> <tr> <td>Metz β-PdD_{0.60}</td> <td>296(4)</td> <td>861(9)</td> <td>0.61(4)</td> <td>99(1)</td> </tr> </tbody> </table>			sample	θ [Pd] (K)	θ [D] (K)	Strain (%)	D (Å)	Pd metal	324(2)	-	0.57(1)	-	α -PdD _x	329(3)	-	0.48(1)	-	β -PdD _x	302(2)	849(5)	0.75(2)	-	Metz β -PdD _{0.60}	296(4)	861(9)	0.61(4)	99(1)
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Experiment report (continued):

Fig. 1 (above)
Lattice Constants
versus temperature

Fig. 2 (above)
Thermal Displacements
versus Temperature

Instrument used: (please type) HIPD	Local contact: G. H. Kwei and J. Eckert	Proposal number: (for LANSCE use only) 900301
Title: Temperature Dependent Neutron Powder Diffraction of [Pt _{en}] ₂ [Pt _{en} ₂ X ₂](ClO ₄) ₄ (X=Cl, Br)		Report received: (for LANSCE use only) 6/11/69
Authors and affiliations: Sara C. Hockett, A. D. F. Bulou, G. H. Kwei, <u>B. I. Swanson</u>		
Experiment report: Abstract for article to be submitted to <i>Inorganic Chemistry</i> : <p>The temperature dependence of [Pt_{en}]₂[Pt_{en}₂X₂](ClO₄)₄ structures (PtX where en= H₂NCH₂CH₂NH₂; X=Cl, Br) has been studied by pulsed neutron powder diffraction from 11-302 K. PtBr undergoes a monoclinic to orthorhombic phase transformation at 301 K. Measurements at 300, 100, and 11 K show that for the low-temperature monoclinic phase the best structural description is obtained with the space group P2₁/m. Both P2 and P2/m had previously been proposed^{1,2}; the difficulty in unambiguous space group determination for this class of low-dimensional materials is well-established.</p> <p>For PtCl, measurements at 11, 100, 140, and 250 K confirm the choice of P2₁/m for the monoclinic phase of this material as well. PtCl had not previously been observed in the monoclinic form. However, due to facile PtCl/PtBr solid solution formation it had been proposed that a low-temperature PtCl phase isomorphous with monoclinic PtBr existed. The 302 K measurements show that Ibam, as opposed to I222,³ provides the best description for the orthorhombic phase of PtCl (T_c=291K).</p> <p>The effect of temperature and phase change on unit cell parameters and bond distances will be discussed. In particular, it appears that the charge density wave (CDW) in PtBr can be weakened by lowering the temperature. (This softening is calculated in terms of a Δ parameter where $\Delta = \text{Pt}^{\text{IV}}\text{-X}/\text{Pt}^{\text{II}}\text{-X}$ and approaches 1 with decreasing CDW strength.) This result contrasts the expected CDW hardening with decreasing temperature and will be compared to the results of spectroscopic measurements which support this observation.</p>		

Experiment report (continued):

References:

1. Keller, H. J.; Müller, B.; Ledzema, G.; Martin, R. *Acta Cryst.* **1985**, C41, 16.
2. Weinrach, J. B.; Ekberg, S. A.; Conradson, S. D.; Swanson, B. I.; Hochheimer, H. D. *Inorg. Chem.* **1990**, 29, 981.
3. Matsumoto, N.; Yamashita, M.; Ueda, I. Kida, S. *Memoirs of the Faculty of Science, Kyushu Univ., Ser. C* **1978**, 11, 209.

Instrument used (please type)	Local contact:	Proposal number: (for LANSCE use only)
HIPD	R. A. Robinson	900302
Title:		Report received: (for LANSCE use only)
Magnetic Structures of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta}$		6/6/91
Authors and affiliations:		
<p>D. C. Johnston, C. Stassis and X. L. Wang, Physics Dept., Iowa State University, Ames IA 50010, C.-K. Loong, Argonne National Laboratory, Argonne IL 60439, and R. A. Robinson, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545.</p>		
Experiment report:		
<p>Recently, D. C. Johnston and co-workers have synthesized two new systems¹, the $\text{La}_2\text{CuO}_{4+\delta}$ ($0.10 \leq \delta \leq 0.42$) and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ ($0.02 \leq x \leq 0.20$, $0.05 \leq \delta \leq 0.50$), by hydrogen reduction and subsequent oxidation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. These materials exhibit either the K_2NiF_4-type T or the Nd_2CuO_4-type T' structure. They demonstrated that the $\text{La}_2\text{CuO}_{4+\delta}$ compounds are insulators with spin-paired holes due to the excess oxygen localized on the out-of-CuO_2-plane oxygen anions, whereas the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ compounds show metallic character. More importantly, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta}$ displays a sharp peak near 50 K in the magnetic susceptibility data, indicative of a possible antiferromagnetic ordering transition (see Fig. 1). This observed $\chi(T)$ is unprecedented in the heavily Sr-doped region of this system.</p>		

Experiment report (continued):

We have investigated the magnetic structures of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_{4+\delta}$ at low temperatures ($T < 50$ K) by neutron powder diffraction at LANSCE using the HIPD Diffractometer. To within experimental uncertainties we find no evidence of magnetic reflections. Since the feasibility for this type of measurements has been demonstrated by recent studies² of Bi_2CuO_4 , we concluded that the anomalous temperature dependence of the susceptibility of this compound is not due to long-range magnetic ordering of the Cu spins. However, short-range spin ordering and/or fluctuations such as spin glass behavior cannot be ruled out.

References:

1. J. H. Cho, F. C. Chou, and D. C. Johnston, preprint (submitted to Phys. Rev. Lett.).
2. E. W. Ong, G. H. Kwei, R. A. Robinson, B. L. Ramakrishna, and R. B. Von Dreele, preprint.

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
HIPD	A. C. Lawson	900303
Title:		Report received: <i>(for LANSCE use only)</i>
Magnetic and Structural Properties of UPdSn		1/8/91
Authors and affiliations:		
<p>R. A. Robinson, LANSCE, LANL A. C. Lawson, MST Division, LANL K. H. J. Buschow, Philips Research Labs., Eindhoven</p>		
Experiment report:		
<p>In 1989, we took some magnetic diffraction data [1] on the ternary compound UPdSn, above and below its supposed Néel temperature, 29K. The magnetic peaks could all be indexed in a double-sized orthorhombic cell, but we showed that there was no collinear magnetic structure that would give the complete set of observed reflections. The magnetic space group analysis of Prandl[2] only allows collinear structures, for the uranium site in the reported structure (in space group P6₃/mmc). Nevertheless, we tried some simple coplanar non-collinear structures which, while giving intensity in all the observed reflections, gave very poor agreement with the intensities.</p> <p>Then, in early 1990, we became aware of some new susceptibility data (due to de Boer and Sechovsky, and reported in Ref. 3), which showed that there were two separate magnetic transitions at approximately 25K and 40K. We therefore took some more neutron diffraction data on HIPD between these two transitions, to identify the new magnetic phase and elucidate the low-temperature magnetic structure. We were successful in both these aims and our main conclusions are as follows:</p> <ol style="list-style-type: none"> 1. We have shown that the crystallographic structure has the non-centric GaGeLi structure type, in the space group P6₃mc, rather than the CaIn₂ structure type (in P6₃/mmc) reported previously. This allows Pd/Sn order (they are disordered in the CaIn₂ structure type). While the contrast between Pd and Sn atoms is so weak that we cannot tell which atom lies on which site, there are clearly two distinct sites and we presume the larger Sn atom to be on the site with more room. 2. The magnetic structure (Phase I) between 25K and 40K, is shown in the Figure, with $\phi = 54^\circ$ and θ at or close to 0°. It is interesting to note that this magnetic structure is allowed by a space group analysis for P6₃mc, whereas it would not be allowed for the CaIn₂ structure! 3. For the magnetic structure (Phase II) below 25K, the moments rotate out of the orthorhombic b-c plane to give the structure shown in the Figure, with $\phi = 54^\circ$ and $\theta = 45^\circ$. 4. At the lowest temperature, the uranium moment is $2.05 \pm 0.13 \mu_B$. 		

Experiment report (continued):

This work has been written up as Ref. 3 and submitted to J. Magn. Magn. Mater.

Figure. The magnetic structure in Phase II (less than 25K) of UPdSn, in the orthorhombic magnetic cell. The hexagonal crystallographic cell is shown by the dashed lines. The structure of Phase I ($25\text{K} < T < 40\text{K}$) can be obtained by setting $\theta = 0$, so that the moments all lie in the b-c plane.

References:

- [1] R. A. Robinson, A. C. Lawson and K. H. J. Buschow, LANSCE Experimental Report D-10.0, in Los Alamos Progress Report LA-11933-PR (1990) p.4.
- [2] W. Prandl, in "Neutron Diffraction", ed. H. Dachs, Springer-Verlag, Berlin 1978, p.113.
- [2] R. A. Robinson, A. C. Lawson, K. H. J. Buschow, F. R. de Boer, V. Sechovsky and R. B. Von Dreele, submitted to J. Magn. Magn. Mater. (1990), Los Alamos preprint LA-UR-90-3875.

Instrument used: (please type) HIPD	Local contact: R.B. Von Dreele	Proposal number: (for LANSCE use only) 900304
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Title: Determination of Amorphous Component of Silicon Nitride	Report received: (for LANSCE use only) 6/10/91
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Authors and affiliations:

R.B. Von Dreele, LANSCE

J. Cline, Ceramics Div., NIST, Gaithersburg, MD

Experiment report:

Silicon nitride is a high temperature ceramic of considerable industrial interest. The commercially prepared " α - Si_3N_4 " contains β - Si_3N_4 and amorphous Si_3N_4 as contaminants. In the course of developing a Si_3N_4 Standard Reference Material (SRM) for α/β ratio and amorphous content, we have determined the composition of a sample of ' α - Si_3N_4 ' by Rietveld refinement with time-of-flight neutron powder diffraction data collected from a series of four " α - Si_3N_4 "/ β - Si_3N_4 mixtures. The diffraction data from the +153° bank for all four samples was subjected to a simultaneous 2-phase Rietveld refinement with GSAS¹. A plot of the β phase fraction with makeup composition, Fig.1, shows a clear nonlinearity from the amorphous component. Fig. 2 shows a plot which gives the composition from the slope and intercept assuming that pure β - Si_3N_4 is single phase. This analysis gives for this particular sample of " α - Si_3N_4 " 93.8% α - Si_3N_4 , 2.1% β - Si_3N_4 and 4.1% amorphous Si_3N_4 . The structure refinement part of the Rietveld refinement also gave new determinations of the crystal structures of α - Si_3N_4 and β - Si_3N_4 . α - Si_3N_4 has space group $P31c$, $a=7.74692(8)\text{\AA}$, $c=5.61552(8)\text{\AA}$ at 300K; the structure is in essential agreement with that previously reported² from a single crystal x-ray study. β - Si_3N_4 has space group $P6_3/m$, $a=7.59322(36)\text{\AA}$, $c=2.90366(14)\text{\AA}$ at 300K; there is no evidence that the structure has space group $P6_3$ as previously reported³ from single crystal x-ray work.

Fig. 1 Plot of makeup fraction (f_β) vs. phase fraction (S_β) of β - Si_3N_4 from Rietveld refinement

Experiment report (continued):

Fig. 2 Plot of makeup and phase fraction ratios to give α -Si₃N₄ mole fraction as slope and β -Si₃N₄ as negative intercept in pure " α -Si₃N₄".

References:

- ¹A.C. Larson & R.B. Von Dreele, "General Structure Analysis System - GSAS", Los Alamos Laboratory Report, LAUR 86-748 (1990).
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Instrument used: <i>(please type)</i> HIPD- High Intensity Powder Diffractometer	Local contact: Robert VonDreele	Proposal number: <i>(for LANSCE use only)</i> 900305
Title: The Investigation of the Magnetic Structure of $\text{Sr}_{14}\text{MnBi}_{11}$		Report received: <i>(for LANSCE use only)</i> 2/25/91
Authors and affiliations: <p style="text-align: center;">Traci Y. Kuromoto and Susan M. Kauzlarich*</p> <p style="text-align: center;">Department of Chemistry University of California Davis, CA 95616</p>		
Experiment report: <p>The use of neutron diffraction for the study of magnetic ordering phenomenon has been well studied.¹ The growth of diffraction peaks and the evolution of new peaks as the temperature is varied reveals the type of magnetic ordering (ferromagnetic, ferrimagnetic, antiferromagnetic) and in the ferromagnetic case this may also reveal the direction of the magnetic moments. The use of computer fitting programs will also calculate the magnitudes of the individual moments in addition to the information mentioned above.</p> <p>The compound of interest, $\text{Sr}_{14}\text{MnBi}_{11}$, is a ferromagnet with a T_c of about 33K, as deduced from magnetic susceptibility curves.² Using the Curie constant, the moment above T_c is found to be consistent with 4 unpaired electrons/Mn, however, below the ordering temperature, the saturation moment is reduced to 2.3 e/Mn. One possibility for this behavior is that $\text{Sr}_{14}\text{MnBi}_{11}$ is actually a canted ferromagnet with some of its moments oriented on a different axis than others. In contrast, a normal ferromagnet has all of its moments oriented along a single axis. In the simplest case, new diffraction peaks in the diffraction pattern would confirm a canted ferromagnet due to a change in the periodicity of the lattice.</p> <p>Powdered samples of about 10 grams were used for the experiments. Diffraction patterns were obtained at 6 temperatures, 300K, 54K, 39K, 27K, 15K and 10K. These temperatures were chosen to observe the growth of magnetic peaks below the ordering temperature.</p> <p>Attention was given to the higher d-spacing peaks, since magnetic diffraction peaks are more intense in this regime. Therefore, the diffraction pattern obtained from bank no. 5 (two-theta=39.81°) was used and the peaks with d-spacings between 4 and 9 angstroms were studied in detail.</p> <p>No new peaks were observed below the magnetic ordering temperature which may indicate that $\text{Sr}_{14}\text{MnBi}_{11}$ is a normal ferromagnet. To obtain information on the direction of the ordered moments, the growth in intensity of some of the diffraction peaks was studied. Powder diffraction patterns were calculated using data obtained from single crystal X-ray diffraction.³ A diffraction pattern was calculated for the entire structure and one for the Mn lattice alone. Assuming that the magnetic moments originate from the manganese atoms alone, observed changes should occur mainly in the diffraction peaks resulting from only the Mn atoms. Therefore, these diffraction peaks were picked out from the neutron diffraction pattern, and studied as a function of temperature.</p>		

Experiment report (continued):

The relative intensities of 5 diffraction peaks were obtained from the GSAS program and normalized to a peak which resulted from non-manganese atoms. In this way, we could minimize effects due to background scattering. A plot of the intensity versus temperature for these 5 peaks is shown in Figure 1. The peak located at 4.5 Å doesn't show any significant temperature dependence. The peaks at 4.9 Å, 5.07 Å, 8.6 Å and 8.9 Å show the most significant temperature dependent behavior. The 5.07 Å peak is shown on an expanded intensity scale in Figure 2. This peak displays a linear temperature dependence both above and below 33K with a sharp break consistent with the magnetic ordering temperature. The fact that this type of behavior is not observed in the intensities of other peaks seems to indicate that ordering may occur along one of the directions that correspond to the hkl values of these peaks.

Figure 1. Corrected Intensity vs. Temperature (K). Figure 2. Corrected Intensity vs. Temperature (K) for the Peak at 5.07 Å.

The conclusions drawn thus far from the neutron diffraction experiments are as follows: 1) the neutron diffraction experiments suggest that $\text{Sr}_{14}\text{MnBi}_{11}$ may be a normal ferromagnet and not a canted ferromagnet, and 2) comparison of the peak intensities above and below the ordering temperature provide a possible direction of the ordered moments.

Further study will concentrate on the fitting of the diffraction patterns using the new magnetic GSAS program provided by Robert VonDreele and Los Alamos. If successful, the low temperature magnetic moment and magnetic lattice can be obtained.

References:

1. Y.A. Izyumov and R.P. Ozerov, Magnetic Neutron Diffraction, Plenum Press, New York, 1970.
2. a) D.J. Webb, T.Y. Kuromoto and S.M. Kauzlarich, J. Magn. Magn. Mat., in press. b) T.Y. Kuromoto, S.M. Kauzlarich and D.J. Webb, Mol. Cryst. Liq. Cryst., 181, 349-357.
3. C.M. Clark, D.K. Smith, and G.J. Johnson, A FORTRAN II program for calculating X-ray diffraction patterns- version 5. Department of Geosciences, Pennsylvania State University, University Park, PA 1973.

Instrument used: <i>(please type)</i> HIPD- High Intensity Powder Diffractometer	Local contact: Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900306
Title: Structural Investigation of $\text{La}_{1-x}\text{Sr}_x\text{TiO}_{3\pm y}$ ($x = 0.05, 0.30, 0.50$)		Report received: <i>(for LANSCE use only)</i> 2/25/91
Authors and affiliations: <p style="text-align: center;">Joseph E. Sunstrom IV and Susan M. Kauzlarich* Department of Chemistry University of California Davis, California 95616</p>		
Experiment report: <p>A set of requirements has been proposed for high T_c superconductivity in metal oxide compounds.¹ These rules are based on features common to both copper and bismuth oxides. The superconducting compounds in these systems are mixed valent metal oxides which have either a fraction of one hole (Cu d^9) or one electron (Bi s^1) in the electronic shell of the metal. There should be a single e^- state which in a d^1 or d^9 compound is attained through low symmetry crystal structures. Presently, there are no high T_c superconductors based on a d^1 metal oxide.</p> <p>A study of mixed valent titanium oxide compounds² has been initiated in order to investigate the characteristics mentioned above as prerequisites for superconductivity. LaTiO_3 (GdFeO_3 structure) is an orthorhombically distorted perovskite compound.³ The LaTiO_3 structure consists of a Ti-O octahedra which are corner shared in three dimensions with La^{3+} interspersed between them. The La^{3+} is too small for the twelve coordinate site on which it sits, so the Ti-O octahedra are buckled in order to make La^{3+} eight coordinate. By doping Sr^{2+} into LaTiO_3, a mixed valent titanium oxide can be made which has a fraction of an electron in the d shell of titanium. Since Sr^{2+} is larger than La^{3+}, the Ti-O octahedral network becomes less distorted.</p> <p>The solid solution $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ ($0 \leq x \leq 0.50$) has been prepared and structurally characterized using Guinier powder X-ray diffraction. The compounds could be indexed on an orthorhombic cell (Pbnm) for $x \leq 0.30$. The samples $x = 0.40, 0.50$ could be indexed on a cubic cell, but because of broad peaks were better indexed as tetragonal. A plot of cell volume vs. composition shows a change in slope at $x = 0.10$ which is a deviation from Vegard's law that indicates some structural change. The deviation from Vegard law is due to the changes in the a and b cell parameters which approach each other until $x = 0.10$ then diverge. Room temperature</p>		

Experiment report (continued):

neutron diffraction data were collected on three samples ($x = 0.05, 0.30, 0.50$) in order to determine the nature of the structure change at $x = 0.10$, to decide if the $x = 0.50$ sample is cubic or tetragonal, and to examine the changing Ti-O-Ti angle which is a critical parameter in the properties of these materials.⁴

The data were refined using the GSAS program provided by LANSCE. The refined lattice parameters were in good agreement with those obtained from Guinier techniques. The atomic positional parameters and isotropic temperature factors were refined to convergence. Corrections were made for both absorption and extinction in the samples. The $x = 0.05, 0.30$ samples were refined in the space group Pbnm to Rp values of 4.9% and 7.3% respectively. The $x = 0.50$ sample could not be satisfactorily refined in the space groups: Pbnm, Pm3m, P4mm, and Pbn2₁.

A structural model obtained by refinement of the $x = 0.05, 0.30$ samples can explain the Vegard's law deviation at $x = 0.10$. The structure has two crystallographically distinct oxygens (O1, O2) and three different Ti-O distances (Ti-O1 along c) and (Ti-O2a, Ti-O2b in the ab plane). Upon doping with Sr²⁺, the two Ti-O2 distances approach one another, then at $x = 0.10$ they get farther apart. This model is consistent with the changes in the lattice parameters. There are several competing effects which could account for this distortion. Ionic radii on the La(Sr) site is becoming larger and the average electronegativity is decreasing. The Ti³⁺ is also being replaced by smaller Ti⁴⁺.

The Ti-O-Ti angle in LaTiO₃ is 154°, but should approach 180° (SrTiO₃) with increasing Sr content. The structural models also indicate that this is true. The properties of perovskite compounds have been described in terms of a transfer integral b which is related to the Ti-O-Ti angle.⁵ As the angle approaches 180°, maximum overlap between the Ti t_{2g} and O 2p orbitals (conduction band) is achieved. The goal is to get as close to 180° as possible while maintaining the distorted structure.

Attempts to refine the $x = 0.50$ sample included using the higher symmetry space groups of cubic SrTiO₃ (Pm3m) and tetragonal BaTiO₃ (P4mm). The data set had additional peaks which were not consistent with the higher symmetry space groups. The lower symmetry space groups, Pbn2₁ and Pbnm, did not give an acceptable refinement. These additional peaks could be due to impurities or a second phase. The data has not been refined as a two phase system and further refinement has not been pursued.

The neutron diffraction study of $x = 0.05, 0.30$ will be used to explain the nature of the Vegard's law deviation in an upcoming publication on the series.

References:

1. A. W. Sleight, in "High Temperature Superconducting Materials", W. E. Hatfield and J. H. Miller Jr., Ed., (Marcel Dekker 1988) 1.
2. S. M. Kauzlarich, J. E. Sunstrom, IV and P. Klavins in "The Chemistry of Electronic Ceramic Materials", NIST SP 804, P. K. Davies, R. S. Roth and R. J. Cava, eds. (1991).
2. M. Eitel and J. E. Greedan, *J. Less-Common Met.*, 116 (1986) 95.
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4. J. B. Goodenough, *Prog. Solid State Chem.*, 5 (1971) 145.

Instrument used: (please type) HIPD	Local contact: Dr R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900307
Title: Magnetic Structure Determination of α -Fe ₂ PO ₅		Report received: <i>(for LANSCE use only)</i> 3 / 7 / 91
Authors and affiliations: J.K. Warner, Chemical Crystallography Laboratory, Oxford, UK. A.K. Cheetham, Chemical Crystallography Laboratory, Oxford, UK. R.B. Von Dreele LANSCE.		
Experiment report: <p> α-Fe₂PO₅ is a mixed valence compound (S.G.= <i>P n m a</i>, $a=7.378\text{\AA}$, $b=6.445\text{\AA}$, $c=7.471\text{\AA}$, $Z=4$) in which Fe²⁺ and Fe³⁺ are located in two different crystallographic sites. The octahedra surrounding Fe²⁺ form chains parallel to the <i>b</i>-axis and share edges. The octahedra containing Fe³⁺ are connected on both sides of these chains, alternating with the PO₄ tetrahedra. Each Fe³⁺ octahedra shares two faces with Fe²⁺ octahedra. Figure 1 shows the structure of the chains of iron octahedra. An antiferromagnetic phase transition occurs in this material at around 250K. Neutron powder data were collected on HIPD at 300K and below the Néel temperature at 12K. Figure 2 shows the normalized counts/μs obtained at the 40° detector bank at 300K and 12K. The additional intensity in the low temperature profile is due to the magnetic ordering of the iron. All the magnetic peaks can be indexed on the same size cell as the nuclear structure, with the strongest magnetic peak corresponding to the (100) reflection. Refinement of various magnetic models using GSAS is proceeding. </p> <p> Experimental assistance was provided by Dr R.B. Von Dreele. The work has benefited from the use of facilities at the Manuel Lujan, Jr. Neutron Scattering Center, a national user facility funded as such by the DOE/Office of Basic Energy Sciences. J. Warner would like to thank the Association of Commonwealth Universities for the provision of a Commonwealth Scholarship and travel funds. </p>		

Experiment report (continued):

Figure 1. Structure of the chains of Fe octahedra running parallel to the b -axis in α -Fe₂PO₅. The large circles indicate Fe³⁺ and the smaller circles indicate Fe²⁺.

Figure 2. Normalised counts/ μ s obtained at the 40° detector bank at 300K and 12K for α -Fe₂PO₅ on HIPD.

References:

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
HIPD	Dr R.B. Von Dreele	900308
Title: Magnetic Structure Determination of Some Transition Metal Phosphates		Report received: (for LANSCE use only) 3/7/91
Authors and affiliations: J.K. Warner, Chemical Crystallography Laboratory, Oxford, UK. A.K. Cheetham, Chemical Crystallography Laboratory, Oxford, UK. A.G. Nord, Riksanstikvaricambetet och Statens Historiska Museer, Stockholm, Sweden. R.B. Von Dreele LANSCE. M. Yethiraj. LANSCE.		
Experiment report: <p>A series of transition metal phosphates isostructural with the mineral <i>sarcopside</i> (space group $P2_1/c$) have been shown to possess some very interesting magnetic properties. The structure consists of chains of edge-shared octahedra, similar to those of <i>olivine</i>, but with every fourth octahedron missing. This leaves a chain of three octahedra containing two unique cation sites, the central M1 cation possessing a fairly regular symmetry and smaller volume compared with the distorted M2 sites of the two terminal octahedra. $Ni_3(PO_4)_2$ is readily formed in this structure by solid state reaction under atmospheric conditions and $Fe_3(PO_4)_2$ is formed under high pressure hydrothermal conditions.</p> <p>Neutron powder data were collected on HIPD using the Displex closed cycle refrigerator on $Ni_3(PO_4)_2$ at 10.1K, and above the antiferromagnetic transition ($T_N=18K$) at 20K. Below T_N, reflections of purely magnetic origin were observed, the strongest being the $(0\ 1/2\ 1)$. The magnetic cell has twice the volume of the nuclear cell, being doubled along the <i>b</i>-axis, and requires a symmetry of P-1 or lower to index all of the magnetic reflections. Preliminary analysis indicates opposing spin directions on the M2 sites at either end of the chain. Various magnetic models using collinear spin directions have been tried, and analysis is continuing with possible non-collinear structures.</p> <p>Data were also collected on a 0.5g sample of $Fe_3(PO_4)_2$, ($T_N=44K$) at 10.1K and 59.7K. Intensity due to magnetic reflections was found superimposed upon nuclear peaks below T_N, with the strongest magnetic peak corresponding to the (011). Figure 1 shows the observed and calculated profiles for (i) the nuclear structure at 59.7K and (ii) the nuclear and magnetic structure, at 10.1K. Preliminary analysis shows that there is no net moment on the M1 site, confirming the findings of an earlier Mossbauer study¹. This can be rationalized crystallographically as the symmetric M1 site occupies the special position of $(1/2,0,0)$. The centre of inversion at this site allows two possibilities for the magnetic moment, either zero or the full moment depending upon the magnetic symmetry. The spin directions on M2 at either end of the chain are opposite, with a moment of around 2.1 B.M. parallel to the <i>a</i>-axis. This</p>		

Experiment report (continued):

value for the average moment is lower than expected for Fe^{2+} , and may be a result of the disorder on the M1 sites, or indicate a more complex, non-collinear structure. Figure 2 shows the structure of $\text{Fe}_3(\text{PO}_4)_2$ with the magnetic spin directions on the iron sites. This analysis is limited by the resolution and nature of the powder data, and a single crystal study of these materials, and particularly their field dependant effects, would be of great interest.

All the structural refinements were carried out using the version of GSAS modified for magnetic structures by Dr M. Yethiraj. Experimental assistance was provided by Dr R.B. Von Dreele. The work has benefited from the use of facilities at the Manuel Lujan, Jr. Neutron Scattering Center, a national user facility funded as such by the DOE/Office of Basic Energy Sciences. J. Warner would like to thank the Association of Commonwealth Universities for the provision of a Commonwealth Scholarship and travel funds.

Figure 1. Observed and calculated profiles of $\text{Fe}_3(\text{PO}_4)_2$ at (i) 59.7K and (ii) 10.1K.

Figure 2. The structure of the Fe octahedra in *sarcopside* showing the direction of spin on the magnetically ordered M2 sites. The paramagnetic M1 sites are shown as black dots.

References:

1. T. Ericsson and A.G. Nord, American Mineralogist 69, 889-95 (1984).

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900309.0
Title: Variable Temperature Study of Phase Transitions in KD_2PO_4		Report received: <i>(for LANSCE use only)</i> 2/6/91
Authors and affiliations: R.B. Von Dreele, LANSCE, MS H805, Los Alamos National Laboratory, Los Alamos, NM, 87545 D. Partin, Dept. of Chemistry, Arizona State University, Tempe AZ, 85287		
Experiment report: <p>We attempted a study of the phase transitions in deuterated KH_2PO_4, however the sample contained some contaminating phase and that part of the work was not continued. Instead we performed a preliminary room temperature investigation of the protonated KH_2PO_4 to determine the feasibility of working with protonated materials. Sufficient KH_2PO_4 (VWR Scientific) was placed in a 2mm diameter thin wall fused silica tube so that the sample was ~50mm high and weighed 324mg. A neutron diffraction pattern was collected on HIPD in 3.19hrs (267.8μA-hrs) with the sample at the ambient temperature of the diffractometer (~300K). The data taken in the two detector banks at $\pm 153^\circ 2\theta$ with $d \geq 0.6\text{\AA}$ were subsequently analyzed using the Rietveld method with GSAS[1]. Despite the relatively high background from the incoherent scattering by hydrogen (Fig.1), the refinement proceeded smoothly and gave atomic coordinates (Table 1) that essentially are identical to those given in the literature based on a single crystal neutron study including the anisotropic thermal motion of the H-atom[2]. The latter shows the effect of a probable random displacement toward either O-atom in the hydrogen bond. The residuals for the final refinement are $R_{\text{wp}}=2.97\%$, $R_p=1.91\%$ and $\chi^2=1.346$ for 8370 observations and 43 variables. The final fit to part of the data can be seen in Fig.2 and a drawing of the crystal structure can be seen in Fig 3.</p>		
<p>KH2PO4 324MG AT 300K BANK 1, 2-THETA 153 4, L-S CYCLE 28 OBSD AND DIFF PROFILES</p>		
Figure 1. Observed and calculated intensities for KH_2PO_4 . A difference curve and reflection positions are also shown.		

Experiment report (continued):

Table 1. Structural parameters for KH_2PO_4

Space group $I4_2d$ $a=7.45276(14)\text{\AA}$, $c=6.97171(26)\text{\AA}$

$U_{\text{iso}}(\text{K}) = 0.0269(13)$, $U_{\text{iso}}(\text{P}) = 0.0143(9)$

$x(\text{O}) = 0.014734(21)$, $y(\text{O}) = 0.08365(29)$, $z(\text{O}) = 0.12531(35)$, $U_{\text{iso}}(\text{O}) = 0.0162(5)$

$x(\text{H}) = 0.1489(6)$, $U_{11}(\text{H}) = 0.0211(21)$, $U_{22}(\text{H}) = 0.064(41)$, $U_{33}(\text{H}) = 0.0356(27)$, $U_{23}(\text{H}) = -0.04(4)$

Figure 2. Detail of the fit from the final refinement for KH_2PO_4 . Observed and calculated intensities are shown with the calculated background from the refinement subtracted from both. A difference curve and reflection positions are also shown.

Figure 3. Drawing of the crystal structure of KH_2PO_4 . The ellipsoids are drawn as 75% probability surfaces.

References:

- [1] A.C. Larson and R.B. Von Dreele, "GSAS - General Structure Analysis System", LAUR 86-748, Los Alamos National Laboratory Report.
- [2] S.W. Peterson, H.A. Levy and S.H. Simonsen, J. Chem. Phys. 21, 2084 (1953).

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)			
HIPD	A. C. Lawson	900311.0			
Title: ATTEMPT to MEASURE PHASE FRACTIONS in a Ce_3Al ALLOY		Report received: (for LANSCE use only) 1/25/91			
Authors and affiliations:					
<p>A. C. Lawson and T. Zocco, MST-5 R. B. Von Dreele, LANSCE Los Alamos National Laboratory Los Alamos NM 87545</p> <p>J. M. Lawrence Department of Physics University of California Irvine CA 92717</p>					
Experiment report:					
<p>During the course of a recent electron microscopic examination of Ce_3Al, we raised the question of a possible amorphous component in the alloy. We decided to try quantitative phase analysis using neutron diffraction.</p> <p>The diffraction standards were cylindrical pieces of niobium metal. Three runs each of approximately 1 hour's duration were completed on HIPD, and the patterns were analyzed using GSAS. The essential results are given in the accompanying tables.</p>					
TABLE 1 - Crystal Data					
Material	Structure type	Unit Cell Volume ($\text{\AA}^3$)	absorption (cm^{-1}) at 1 $\text{\AA}$		
Ce_3Al	Ni_3Sn -type	231.	0.0092		
Nb	W-type	35.8	0.0642		
TABLE 2 - Diffraction Data					
Run	Ce_3Al		Niobium		
	Scale	Volume (cm^3)	Scale	Volume	Scale (Corrected)
1383	0.24	0.258	0.0	0.0	0.0
1384	0.25	"	0.42	0.037	0.20
1385	0.22	"	0.63	0.074	0.30

Experiment report (continued):

The phase volumes are proportional to the product of the GSAS scale factor and the cell volume. We tabulate the ratios of the phase volumes (by diffraction) to the measured volumes. This number should be constant - an instrumental characteristic of HIPD.

TABLE 3 - Volume Ratios

Run	Ce ₃ Al	Niobium	Niobium (Corrected)
1383	215	-	-
1384	224	406	194
1385	197	305	145

These numbers would appear to indicate that only about half the Ce₃Al is crystalline. However, this observation is at distinct variance with the electron microscopic observations, and the volume fractions in Table 3 are not at all consistent. Evidently, there is a substantial systematic effect that this analysis has neglected.

Our best guess is that the culprit is our use of inhomogeneous solid samples, i.e., individual pieces of Ce₃Al and Nb. Differences in absorption are not accommodated by the average absorption coefficient used in GSAS. The last column in Tables 2 and 3 shows a simple relative correction to the niobium for this effect using calculated absorption coefficients and the assumption that each material is a sphere. The shape assumption is particularly crude, since actually the Nb is a thin disc and the Ce₃Al is hemispherical. Our approximate correction improves the agreement between the volume ratios in Table 3, but it is not good enough to address the question of the amorphous content of Ce₃Al with any confidence. It is clear that the use of inhomogeneous samples for this type of study must be done with careful attention to sample geometry.

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900313																																																																																																				
Title: Structure of acetanilide, C ₆ D ₅ NHCOCH ₃		Report received: <i>(for LANSCE use only)</i> 6/27/91																																																																																																				
Authors and affiliations: R. Von Dreele, LANSCE, MS H805, Los Alamos National Laboratory J. Eckert, LANSCE, MS H805, Los Alamos National Laboratory																																																																																																						
Experiment report: <p>As part of our investigation of the small sample capabilities for neutron powder diffraction on HIPD, we examined a 129mg sample of C₆D₅NHCOCH₃ contained in a 2mm quartz capillary at 300K for 19.5hr (1504μA-hr) on HIPD. Data taken in the ±153° (d≥1.0Å), -90° (d≥1.375Å) and ±40° (d≥1.50Å) detector banks was used in a Rietveld refinement of the crystal structure with independent isotropic thermal parameters to give the results shown in Table 1. The fit for the +153° data is shown in Figure 1. A set of 19 "soft constraints" for all the chemical bonds within the molecule was included as an additional data set. A Fourier map (Figure 2) calculated from the extracted structure factors gives a very impressive view of the scattering density for this molecule. Figures 3 & 4 show ORTEP sketches of the structure. It is very clear from this result that the amide hydrogen atom, H(11), resides exclusively on N(9) and forms a hydrogen bond with a neighboring molecule to O(10).</p> <p>Table 1. Structure of d₆-acetanilide</p> <p>Space group P b c a, a=19.556(7)Å, b=9.4515(30)Å, c=7.9495(25)Å</p> <table border="1"> <thead> <tr> <th>Atom</th> <th>x</th> <th>y</th> <th>z</th> <th>U_{iso}, Å²</th> </tr> </thead> <tbody> <tr><td>C(1)</td><td>0.4060(4)</td><td>0.0705(8)</td><td>0.1320(9)</td><td>0.047(3)</td></tr> <tr><td>C(2)</td><td>0.3478(5)</td><td>-0.0131(10)</td><td>0.1666(11)</td><td>0.064(4)</td></tr> <tr><td>C(3)</td><td>0.2825(5)</td><td>0.0042(10)</td><td>0.1016(13)</td><td>0.092(4)</td></tr> <tr><td>C(4)</td><td>0.2705(6)</td><td>0.1283(11)</td><td>0.0124(10)</td><td>0.076(4)</td></tr> <tr><td>C(5)</td><td>0.3249(5)</td><td>0.2168(10)</td><td>-0.0327(11)</td><td>0.072(4)</td></tr> <tr><td>C(6)</td><td>0.3922(5)</td><td>0.1899(9)</td><td>0.0250(10)</td><td>0.056(3)</td></tr> <tr><td>C(7)</td><td>0.5278(5)</td><td>0.1270(9)</td><td>0.2119(11)</td><td>0.057(3)</td></tr> <tr><td>C(8)</td><td>0.5853(6)</td><td>0.0665(10)</td><td>0.3087(10)</td><td>0.068(4)</td></tr> <tr><td>N(9)</td><td>0.4709(4)</td><td>0.0543(6)</td><td>0.2004(7)</td><td>0.060(2)</td></tr> <tr><td>O(10)</td><td>0.5211(6)</td><td>0.2564(8)</td><td>0.1783(13)</td><td>0.095(5)</td></tr> <tr><td>H(11)</td><td>0.4782(8)</td><td>-0.0455(10)</td><td>0.2399(13)</td><td>0.038(5)</td></tr> <tr><td>D(12)</td><td>0.3683(6)</td><td>-0.1007(9)</td><td>0.2457(13)</td><td>0.122(5)</td></tr> <tr><td>D(13)</td><td>0.2436(6)</td><td>-0.0608(11)</td><td>0.1443(14)</td><td>0.110(5)</td></tr> <tr><td>D(14)</td><td>0.2256(6)</td><td>0.1468(9)</td><td>-0.0402(12)</td><td>0.095(4)</td></tr> <tr><td>D(15)</td><td>0.3196(7)</td><td>0.2898(9)</td><td>-0.1260(14)</td><td>0.132(6)</td></tr> <tr><td>D(17)</td><td>0.4375(6)</td><td>0.2579(13)</td><td>0.0070(12)</td><td>0.120(4)</td></tr> <tr><td>H(18)</td><td>0.5901(11)</td><td>0.1108(18)</td><td>0.4298(15)</td><td>0.126(9)</td></tr> <tr><td>H(19)</td><td>0.6249(11)</td><td>0.0583(20)</td><td>0.2296(23)</td><td>0.155(10)</td></tr> <tr><td>H(20)</td><td>0.5784(10)</td><td>-0.0383(13)</td><td>0.3509(21)</td><td>0.084(6)</td></tr> </tbody> </table> <p>Residuals, R_{wp}=1.05%, R_p=0.61%, N_{obs}=11153, χ²= 1.720, N_{var}=173</p>			Atom	x	y	z	U _{iso} , Å ²	C(1)	0.4060(4)	0.0705(8)	0.1320(9)	0.047(3)	C(2)	0.3478(5)	-0.0131(10)	0.1666(11)	0.064(4)	C(3)	0.2825(5)	0.0042(10)	0.1016(13)	0.092(4)	C(4)	0.2705(6)	0.1283(11)	0.0124(10)	0.076(4)	C(5)	0.3249(5)	0.2168(10)	-0.0327(11)	0.072(4)	C(6)	0.3922(5)	0.1899(9)	0.0250(10)	0.056(3)	C(7)	0.5278(5)	0.1270(9)	0.2119(11)	0.057(3)	C(8)	0.5853(6)	0.0665(10)	0.3087(10)	0.068(4)	N(9)	0.4709(4)	0.0543(6)	0.2004(7)	0.060(2)	O(10)	0.5211(6)	0.2564(8)	0.1783(13)	0.095(5)	H(11)	0.4782(8)	-0.0455(10)	0.2399(13)	0.038(5)	D(12)	0.3683(6)	-0.1007(9)	0.2457(13)	0.122(5)	D(13)	0.2436(6)	-0.0608(11)	0.1443(14)	0.110(5)	D(14)	0.2256(6)	0.1468(9)	-0.0402(12)	0.095(4)	D(15)	0.3196(7)	0.2898(9)	-0.1260(14)	0.132(6)	D(17)	0.4375(6)	0.2579(13)	0.0070(12)	0.120(4)	H(18)	0.5901(11)	0.1108(18)	0.4298(15)	0.126(9)	H(19)	0.6249(11)	0.0583(20)	0.2296(23)	0.155(10)	H(20)	0.5784(10)	-0.0383(13)	0.3509(21)	0.084(6)
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Experiment report (continued):

A comparison of these values shows reasonable agreement with the previously published crystal structures determined from single crystal x-ray diffraction studies (Brown, 1966 and Brown & Corbridge, 1954). However, careful examination of the bond distances and angles from the present work shows the loss in accuracy from using powder diffraction data with a high incoherent background although it is suprising that this analysis did succeed as well as shown here. Clearly, this demonstration shows that it is possible to successfully refine moderately complex crystal structures with neutron diffraction data from small samples on HIPD.

Figure 1a & b. The fitted powder diffraction pattern for d_6 -acetanilide from the $+153^\circ$ detector bank of HIPD. The observed and calculated values have been normalized by the incident spectrum. The calculated background has been subtracted from both sets of values. The reflection positions are marked and a difference curve is shown.

Figure 1c. The fitted powder diffraction pattern for d_6 -acetanilide from the $+153^\circ$ detector bank of HIPD as unnormalized values and including the background contribution.

Experiment report (continued):

Figure 2. An "observed" Fourier map slice through the amide group calculated with neutron structure factors extracted from data taken from the +153° detector bank during the last least-squares refinement cycle. Those atoms within 0.5Å of this plane are marked. Negative peaks are H atoms, others are positive.

Figure 3. A view of the acetanilide molecule with isotropic thermal motion surfaces calculated at the 50% level.

Experiment report (continued):

Figure 4. A stereoscopic view of the unit cell and contents for acetanilide.

References:

C.J. Brown (1966). *Acta Cryst.* 21, 442-445.

C.J. Brown & D.E.C. Corbridge (1954). *Acta Cryst.* 7, 711-715.

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
HIPD	R.B. Von Dreele	900317
Title:		Report received: (for LANSCE use only)
The crystal structure of Latrappite $\text{Ca}(\text{Nb,Ti})\text{O}_3$		2/6/91
Authors and affiliations:		
R.B. Von Dreele, LANSCE, MS H805, Los Alamos National Laboratory, Los Alamos, NM 87545		
J.E. Post, Dept. of Mineralogical Sciences, Smithsonian Institution, Washington, DC 20560		
Experiment report:		
<p>To explore the feasibility of performing neutron powder diffraction on small samples and to determine the structure of the rare Nb containing mineral Latrappite, we examined a 23mg sample (#156141) collected from Oka, Quebec for 7.13hrs (551.4$\mu\text{A-hr}$). The sample was contained in a 2mm diameter thin wall fused silica tube to give a sample height of ~5mm. Despite the relatively poor quality of the diffraction pattern (Fig. 1) it could be subjected to a Rietveld refinement to give the structure as a common orthorhombic distortion of perovskite (Table 1). The final refinement used both data sets from the $\pm 153^\circ 2\theta$ detector banks for $d \geq 0.6\text{\AA}$. The residuals from the final refinement were $R_{\text{wp}}=8.63\%$, $R_p=5.48\%$, $\chi^2 = 1.182$ for 8384 observations and 43 variables. A drawing of the unit cell contents is shown in Figure 2. The lattice parameters and the site fraction for the Nb atom, 0.265(14), is in good agreement with that expected for a Latrappite that is relatively poor in Nb[1].</p> <p>Table 1 Structural parameters for Latrappite #156141 Space Group $Pbnm$, $a = 5.4280(8)\text{\AA}$, $b = 5.4987(8)\text{\AA}$, $c = 7.7198(14)\text{\AA}$ $x(\text{Ca}) = 0.0055(25)$, $y(\text{Ca}) = 0.420(16)$, $x(\text{O}) = 0.0767(18)$, $y(\text{O}) = 0.4822(16)$ $x(\text{O}') = -0.2881(11)$, $y(\text{O}') = 0.2870(11)$, $z(\text{O}') = 0.0394(8)$, $U_{\text{ov}} = 0.0019(9)$</p>		
<p>Figure 1. A portion of the observed and calculated diffraction patterns from Latrappite, $\text{Ca}(\text{Nb,Ti})\text{O}_3$, both normalized by the incident spectrum. A difference curve and reflection positions are also marked.</p>		

Experiment report (continued):

Figure 2. A drawing of the unit cell contents for Latrappite

References:

- [1] E.H. Nickel and R.C. McAdam, Canadian Miner., 683 (1964)

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
HIPD	R.B. Von Dreele	900320
Title:		Report received: (for LANSCE use only)
Neutron Powder Diffraction Study of Sr_2CuO_3		5/31/91

Authors and affiliations:

D. E. Partin Department of Chemistry, Arizona State University Tempe, Az

G. H. Kwei, Los Alamos National Laboratory, Los Alamos, NM

Experiment report:

Sr_2CuO_3 was synthesized and its structure refined from time-of-flight neutron powder data. The refinement was complicated by the fact that SrCuO_2 was also present in our sample as a minor second phase.

Sr	0.35213(4)	1/2	0	0.0040(1)
Cu	1/2	0	1/2	0.0044(1)
O	0.15465(5)	1/2	0	0.0072(1)
O	0	0	0	0.0060(2)

space group: Immm, $a=12.7003(2)$, $b=3.91107(5)$, $c=3.49885(4)$

$wR_p=3.61$, $R_p=2.51$, and $\chi^2=2.15$

SR2CUO3 IMMM FULL REFINEMENT W/ SR2CUO2 2ND PHASE
BANK 4. 2-THETA -90.0. L-S CIRCLE 179 OBSD AND DIFF PROFILES

Experiment report (continued):

Drawing of the crystal structure of Sr_2CuO_3

References:

- (1) A.C.Larson and R.B.Von Dreele,"GSAS-General Structure Analysis System", LAUR 86-748, Los Alamos National Laboratory Report.
- (2) D.E.Partin,G.H.Kwei,and M.O'Keeffe, in prep.

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900321												
Title: Texture of Stainless Steel - Carbon Steel Laminate		Report received: <i>(for LANSCE use only)</i>												
Authors and affiliations: H. Prißmeyer, GKSS-Geeschacht, Germany R.B. Von Dreele, LANSCE, Los Alamos National Laboratory														
Experiment report: <p>A rolled plate consisting of a three layer laminate with stainless steel outer layers and a carbon steel core was examined on HIPD in several orientations to determine the relative residual stresses in the layers. Analysis of a single diffraction pattern from the $\pm 90^\circ$ detector banks was performed by Rietveld analysis to give the apparent lattice parameters for the crystallites sampled in the orientation shown in Figure 1. Thus, the $+90^\circ$ detectors examined the diffraction from crystal planes parallel to the plate and the -90° detectors examined diffraction from planes normal to the plate. A stress free sample of neither steel was examined. The lattice parameters are listed in the Table.</p> <table> <thead> <tr> <th></th> <th>+90</th> <th>-90</th> <th>$\Delta a/a$</th> </tr> </thead> <tbody> <tr> <td>stainless steel</td> <td>3.59081</td> <td>3.60152</td> <td>3.0×10^{-3}</td> </tr> <tr> <td>carbon steel</td> <td>2.87292</td> <td>2.86758</td> <td>-1.9×10^{-3}</td> </tr> </tbody> </table> <p>Both steels show residual stresses in opposite directions so that the stainless steel shows expansion and the carbon steel shows compression normal to the plate relative to the inplane direction. This result is not an absolute measurement of the residual stress because of the lack of stress-free measurements. In addition there are probable systematic errors (on the order of 10^{-4}) from sample position offsets. However, it compares well with other measurements on this material. A similar measurement at a constant wavelength neutron source gave a compression of $-2.6 \pm 0.5 \times 10^{-3}$ for the carbon core and subsequent destructive borehole/strain gauge measurements also gave a similar value. Examination of the fit from the Rietveld refinement (Figure 2) shows that there are remaining displacements of the reflections from the positions derived from the cubic parameters given above. These differences arise from the different Young's moduli for different directions in the crystallites. No attempt was made to extract this information, however it is quite evident that it could be given an appropriate model for these displacements that can be used in a Rietveld refinement.</p>				+90	-90	$\Delta a/a$	stainless steel	3.59081	3.60152	3.0×10^{-3}	carbon steel	2.87292	2.86758	-1.9×10^{-3}
	+90	-90	$\Delta a/a$											
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carbon steel	2.87292	2.86758	-1.9×10^{-3}											

Experiment report (continued):

Figure 1. Orientation of steel laminate in HIPD

Figure 2. Observed and calculated powder diffraction profiles for steel laminate for the +90° detector bank on HIPD. The calculated background from the refinement has been subtracted from both curves. The lower row of marks gives the reflection positions for the stainless steel and the upper set are for the carbon steel. A difference curve is also shown.

References:

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900325
Title: Neutron Powder Diffraction Study of BaCuO_2 at Low Temp.		Report received: <i>(for LANSCE use only)</i> 5/31/91
Authors and affiliations: D. E. Partin and M. O'Keeffe Department of Chemistry Arizona State University Tempe, Az 85287		
Experiment report: <p>The diffraction pattern collected at 10K was identical to the one collected at 300K, so the data was not refined.</p>		

Experiment report *(continued)*:

BACUO2 AT 10K

BANK NO. = 1 TWO-THETA = 153.43

OBSERVED PROFILE

References:

D.E.Partin,M.O'keeffe, work in progress.

Instrument used: (please type) HIPD	Local contact: Robert Von Dreele	Proposal number: (for LANSCE use only) 900332.0																																												
Title: THE AB INITIO CRYSTAL STRUCTURE DETERMINATION OF CUPT₃O₆ FROM A COMBINATION OF POWDER NEUTRON AND X-RAY DATA.		Report received: (for LANSCE use only) Jan. 7, 1991																																												
Authors and affiliations: J. B. Parise, ESS, SUNY, Stony Brook., J. Hriljac, Physics, BNL, G. Kwei, LANSCE, R. D. Shannon, E.I. Du Pont, and K. Schwartz, RayChem.																																														
Experiment report: <p>In light of their application as chlor-alkali anodes and H₂O₂ fuel-cell electrocatalysts, ternary platinum oxides of the type MPt₃O₆ (M=Co,Ni,Cu) are of considerable technological interest¹⁻³. A range of compositions has been found to crystallize with a common structure¹, with only the copper containing material possessing a unique, and until now undetermined, structure. Since "single" crystals suitable for structure determination were unavailable we have embarked upon structure solution from the powder diffraction data.</p> <p>High resolution x-ray data, collected at the x-7a beamline of the NSLS, displayed a single well resolved, weak, low angle reflection indicating the true space group to be Pn2₁m rather than Pnnm as had been previously thought¹⁻³. The positions of the heavy atoms (Table 1) were found using the x-ray data and manual interpretation of a Patterson map. The oxygens were found, and the complete structure refined, using neutron data collected on the HIPD at LANSCE. The refined atomic positional parameters and selected interatomic distances are given in Tables 1 and 2, respectively.</p> <p>Table 1. Refined atomic positional parameters for CuPt₃O₆ (Pn2₁m, a = 6.1154(1), b = 11.560(1), c = 3.1012(1)Å derived from the neutron powder data; R_{wp}=0.037, R_p=0.023, goodness of fit (χ²) = 2.3.</p> <table border="1"> <thead> <tr> <th>atom</th> <th>x</th> <th>y</th> <th>z</th> </tr> </thead> <tbody> <tr> <td>Pt(1)</td> <td>0.2574(6)</td> <td>1/2</td> <td>0</td> </tr> <tr> <td>Pt(2)</td> <td>0.0929(7)</td> <td>0.2407(5)</td> <td>1/2</td> </tr> <tr> <td>Pt(3)</td> <td>0.4075(8)</td> <td>0.7576(4)</td> <td>1/2</td> </tr> <tr> <td>Cu(1)</td> <td>0.2515(9)</td> <td>0.9985(7)</td> <td>0</td> </tr> <tr> <td>O(1)</td> <td>0.0539(8)</td> <td>0.0647(5)</td> <td>1/2</td> </tr> <tr> <td>O(2)</td> <td>0.3659(9)</td> <td>0.5920(7)</td> <td>1/2</td> </tr> <tr> <td>O(1*)</td> <td>0.4287(9)</td> <td>0.9332(6)</td> <td>1/2</td> </tr> <tr> <td>O(2*)</td> <td>0.1376(9)</td> <td>0.4109(6)</td> <td>1/2</td> </tr> <tr> <td>O(3*)</td> <td>0.2879(5)</td> <td>0.2070(4)</td> <td>0</td> </tr> <tr> <td>O(4)</td> <td>0.0953(6)</td> <td>0.7870(4)</td> <td>1/2</td> </tr> </tbody> </table> <p>In common with other members of the MPt₃O₆-family (M=Co,Ni,Zn,Cd,Mg) the structure of CuPt₃O₆ contains two 6-coordinate Pt⁴⁺ and one</p>			atom	x	y	z	Pt(1)	0.2574(6)	1/2	0	Pt(2)	0.0929(7)	0.2407(5)	1/2	Pt(3)	0.4075(8)	0.7576(4)	1/2	Cu(1)	0.2515(9)	0.9985(7)	0	O(1)	0.0539(8)	0.0647(5)	1/2	O(2)	0.3659(9)	0.5920(7)	1/2	O(1*)	0.4287(9)	0.9332(6)	1/2	O(2*)	0.1376(9)	0.4109(6)	1/2	O(3*)	0.2879(5)	0.2070(4)	0	O(4)	0.0953(6)	0.7870(4)	1/2
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Experiment report (continued):

Table 2. Selected interatomic distances (Å) for CuPt_3O_6

vector	distance
Pt(1)_O(1)	2.045(6)
Pt(1)_O(2)	1.994(5)
Pt(1)_O(2)	1.994(5)
Pt(1)_O(1*)	2.070(7)
Pt(1)_O(2*)	2.001(4)
Pt(1)_O(2*)	2.001(4)
Pt(2)_O(1)	2.049(6)
Pt(2)_O(2*)	1.987(7)
Pt(2)_O(3*)	1.994(4)
Pt(2)_O(3*)	1.994(4)
Pt(2)_O(4)	2.004(3)
Pt(2)_O(4)	2.004(3)
Pt(3)_O(2)	1.931(7)
Pt(3)_O(1*)	2.034(6)
Pt(3)_O(3*)	1.952(6)
Pt(3)_O(4)	1.939(6)
Cu(1)_O(1)	2.109(6)
Cu(1)_O(1)	2.109(6)
Cu(1)_O(1*)	2.037(5)
Cu(1)_O(1*)	2.037(5)

4-coordinate Pt^{2+} per asymmetric unit. This mixed valence can be represented as $\text{IV}[\text{Cu}^{2+}]\text{IV}[\text{Pt}^{2+}]\text{VI}[\text{Pt}^{4+}]\text{O}_6$.

In contrast to the other compounds, the divalent counterion Cu^{2+} , is found to be 4-coordinate rather than 8 (Mg, Mn, Co, An, Cd) or 6 (Ni). A comparison of the Zn- and Cu-structure types is presented in Figure 1. In both materials, the Pt^{4+} octahedra are edge-linked to form chains along [001]. In the Zn compound these chains are corner-linked to form sheets in (010), and the sheets are held together by the divalent Pt and Zn ions. In CuPt_3O_6 , the chains are again corner linked but this time form buckled slabs approximately in (100). Again these slabs are held together by the divalent cations.

References:

1. K. B. Schwartz and J. B. Parise J. Phys. Chem. Sol 43, 911 (1982)
2. K. B. Schwartz and C. T. Prewitt, J. Phys. Chem Sol 45, 1-21 (1984)
3. K. B. Schwartz, J. B. Parise, C. T. Prewitt and R. D. Shannon Acta Crystallog. B39, 217 (1983)

Instrument used: <i>(please type)</i> HIPD	Local contact: G.H. KWEI	Proposal number: <i>(for LANSCE use only)</i> 900333
Title: COMBINED X-RAY AND NEUTRON DIFFRACTION STUDY OF THE STRUCTURE OF $\text{Ba}_4\text{CaCu}_3\text{O}_x$		Report received: <i>(for LANSCE use only)</i> 3/1/11
Authors and affiliations: K.A. Kubat-Martin, [*] G.H. Kwei, [±] A.C. Lawson, [*] and D.E. Peterson [#] [*] Materials Science and Technology Division [±] Physics Division [#] Exploratory Research and Development Center Los Alamos National Laboratory Los Alamos, NM 87545		
Experiment report: Cation ordering and oxygen stoichiometry of the nonsuperconducting compound $\text{Ba}_4\text{CaCu}_3\text{O}_x$ have been studied by a joint x-ray and neutron powder diffraction experiment. Neutron diffraction data were taken on the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. In contrast to the related phase $\text{Ba}_4\text{YCu}_3\text{O}_{8.5+\delta}$, [1] which was refined in the space group Pm3, we found that the higher symmetry space group Im3m provides a better fit to the diffraction data for $\text{Ba}_4\text{CaCu}_3\text{O}_x$. The cubic unit cell of $\text{Ba}_4\text{CaCu}_3\text{O}_x$ has a perovskite-like configuration, but possesses lattice lengths double those of a usual perovskite cell. A body-centered cube of Ca atoms defines the corners and center of the 8 Å cell. Corner Ca atoms are bridged by linear O-Cu-O groups; the body-centered Ca atom is similarly bridged to body-centered Ca atoms in adjacent cells. Eight Ba atoms, located at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, are centered in perovskite-like subcubes, the corners of which are defined by six Cu atoms and two Ca atoms. In our investigation, neutron data provide most of the structural information desired; however, since the neutron scattering lengths for Ba and Ca are similar, neutron data were used jointly with x-ray data to study the extent of cation exchange between the Ca and Ba sites; the population values converged to yield a Ca site containing approximately 40% Ba and a Ba site containing approximately 10% Ca. These data suggest that the point occupied by $\text{Ba}_4\text{CaCu}_3\text{O}_x$ in the Ba-Ca-Cu-O phase diagram is actually a region of variable Ca and Ba composition.		

Experiment report (continued):

Refinements of neutron data indicate two oxygen sites an $(x,0,0)$ site that is essentially fully occupied, and a $(\frac{1}{4},0,\frac{1}{2})$ site that is approximately 48% occupied. This gives an average stoichiometry of $\text{Ba}_4\text{CaCu}_3\text{O}_{8.86}$ for the compound ($Z=2$) and an effective Cu-O hole concentration of $p = +0.29$. This value lies between those for $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$ ($p = +0.5$, assuming holes are located in the CuO_2 sheets)[2] and the cation- and oxygen-doped La_2CuO_4 systems ($p = +0.15 - +0.18$).[3] Thus, a superficial comparison of these compounds demonstrates that hole concentration is not the only consideration for superconductivity.

The absence of superconductivity in $\text{Ba}_4\text{CaCu}_3\text{O}_{8.86}$ can be rationalized upon examination of the structure. The compound has a cubic Cu-O network consisting of CuO_6 octahedra with "isolated" O1 atoms and edge-shared O2 atoms. The length of 2.035 Å for the Cu-O2 bond is much longer than the typical Cu-O length of 1.93 Å found in most cuprates. On the other hand, the Cu-O1 bond is quite short (1.791 Å). Thus, in addition to the oxygen vacancies, there are two more obstacles to superconductivity in $\text{Ba}_4\text{CaCu}_3\text{O}_{8.86}$: the large size of the Ba^{+2} ions constrains the Cu-O2 distance to a length that is perhaps too long for hole doping, and the proximity of Ca^{+2} to the O1 oxygens helps stabilize the holes on the latter. These structural features suggest that even an increase in the oxygen content of $\text{Ba}_4\text{CaCu}_3\text{O}_{8.86}$ may not provide the continuous O-Cu-O chains needed for superconductivity.

This work has benefitted from the use of the facilities at the Manuel Lujan Jr. Neutron Scattering Center, a national user facility funded as such by the DOE/Office of Basic Energy Sciences.

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- [1] D.M. DeLeeuw, C.A.H.A. Mutsaers, R.A. Steeman, E. Frikkee, and H.W. Zandbergen, Physica C. 158 (1989) 391.
- [2] Y. Tokura, J.B. Torrance, T.J. Huang, and A.I. Nazzari, Phys. Rev. B 38 (1988) 7156.
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Instrument used: <i>(please type)</i> <p style="text-align: center;">HIPD</p>	Local contact: <p style="text-align: center;">Robert Von Dreele</p>	Proposal number: <i>(for LANSCE use only)</i> <p style="text-align: center;">900334.0</p>
Title: <p style="text-align: center;">THE STRUCTURE OF "LALUGA" GARNET FROM JOINT REFINEMENT OF X-RAY AND NEUTRON DIFFRACTION DATA</p>		Report received: <i>(for LANSCE use only)</i> <p style="text-align: center;">1/7/91</p>
Authors and affiliations: <p style="text-align: center;">J. B. Parise, ESS, SUNY, Stony Brook., J. Hriljac, Physics, BNL, G. Kwei, LANSCE, R. D. Shannon and R. L. Harlow, E.I. Du Pont.</p>		
Experiment report: <p>Recent work¹ concerning the additivity of molecular polarizabilities has suggested that the previously published² chemical composition and site chemistry of lathanum-lutetium-gallium garnet (LALUGA) are in error. The reported¹ composition for LALUGA, La_{2.655}Nd_{0.007}Lu_{2.656}Ga_{2.655}O₁₂, differs from the previously published results² for this material, La_{2.26}Nd_{0.04}Lu_{2.63}Ga_{3.07}O₁₂. Dielectric constant measurements performed on this potential laser host, are in agreement with the gallium deficient composition. The concept of additivity of molecular polarizabilities, whereby the molecular polarizability of a complex substance can be broken up into the molecular polarizabilities of simpler substances according to</p> $\alpha_D(M_2MX_4) = 2\alpha_D(MX) + \alpha_D(MX_4)$ <p>has been discussed¹ elsewhere.</p> <p>Powder and single crystal x-ray data have been collected and are to be combined with neutron data collected on the HIPD at LANSCE. Thus far the neutron data have been analyzed and found to be consistent with the analyzed composition. If lutetium is presumed to fully occupy the octahedral site (Lu(2) in Tables 1 and 2) and if the remaining sites are presumed to be fully occupied, then the excess Lu occupies both the La and Ga-sites. Since the scattering lengths of Lu and Ga are almost equal, x-ray data will be used to check this assumption. For the present only the neutron data have been analyzed and the results are presented in Tables 1 and 2. A sample of the fit between observed and calculated data for the 153° data bank below 1.5Å is shown in the figure.</p>		

Experiment report (continued):

Table 1. Refined atomic parameters for LALUGA ($Ia-3d$, $a = 12.9507(3)$ Å derived from the neutron powder data; $R_{wp}=0.029$, $R_p=0.018$, goodness of fit (χ^2) = 1.3.

site				$U_{iso} \times 10^2$
La/Lu(1)	0.125	0.0	0.25	0.38(2)
Lu(2)	0.0	0.0	0.0	0.44(2)
Ga/Lu(3)	0.375	0.0	0.25	0.37(2)
O(1)	0.96887(8)	0.05744(8)	0.15696(8)	1.02(5)

Table 2. Selected interatomic distances (Å) for LALUGA garnet

La/Lu(1)_O(1)x4	2.4686(11)
O(1)x4	2.5597(11)
Lu(2)_O(1)x6	2.2017(10)
Ga/Lu(3)_O(1)x4	1.8663(11)

References:

1. R. D. Shannon et al *J. Appl. Phys.* **67**, 3789 (1990)
2. T. H. Allik et al *Phys. Rev B*, **37**, 9129 (1988)

Instrument used: <i>(please type)</i> HIPD	Local contact: Robert VonDreele	Proposal number: <i>(for LANSCE use only)</i> 3421.0
Title: Investigation of Molecular Interactions in a Thermotropic Liquid Crystal by Neutron Scattering		Report received: <i>(for LANSCE use only)</i> 2. 4. 1.
Authors and affiliations: Thomas Rieker LANSCE, Los Alamos National Lab, Los Alamos, NM 87545		
Experiment report: This neutron scattering experiment probed the molecular ordering present in the various phases of the thermotropic liquid crystal: <div style="text-align: center;"> </div> <p>which exhibits the following phases:</p> <div style="text-align: center;"> $\begin{array}{ccccccc} X & \xrightarrow{69.9} & SC & \xleftarrow{74.5} & SA & \xleftarrow{77.6} & N & \xleftarrow{84.9} & I \\ & \nwarrow 33.8 & \swarrow 38.9 & & & & & & \\ & & SG? & & & & & & \end{array}$ <p>(all temperatures are in °C)</p> </div> <p>Approximately one gram of the above material was contained in a standard vanadium sample can. The sample can was mounted in an oven with a temperature stability of about 0.1 °C. The various phases were investigated as the sample was both heated and cooled.</p> <p>Several interesting observations were made:</p> <p>1) Of great interest is the presence of higher order reflections from the smectic layering in the smectic phases. Figure (c) is a diffraction pattern taken in the smectic A phase. Here strong (001), (002), and (004) reflections which correspond to the peaks at 32.1 Å, 16.1 Å, and 8.06 Å respectively are evident. The relative peak heights are, $I_{(002)}/I_{(001)} = 1/5$ and $I_{(004)}/I_{(001)} = 1/15$. The (003) and (006) reflections are present but not well resolved. The (003) and (006) peak heights appear to be down by two orders of magnitude from the fundamental.</p>		

Experiment report (continued):

It is surprising to observe strong higher order peaks since smectic liquid crystals typically demonstrate only (001) and (002) reflections by X-ray scattering. With the peak height of the (002) down by 1 to 2 orders of magnitude from the fundamental. Indeed this general observation has given rise to the notion of smectic layering as a 'density wave' fluctuation¹. The observation of several strong higher order reflections by neutron scattering indicates that the molecules have a stronger interaction to align into layers than the density wave model indicates. Higher order reflections are realized through the greatly enhanced scattering contrast of the deuterated tails. High resolution X-ray scattering experiments are planned on oriented and powder samples. These X-ray results will be combined with the neutron data in the General Structure Analysis System (GSAS) program to form a model of the smectic phases.

2) There is an unexpected peak (and higher order reflections) which undergoes a dramatic shift in position from 24.8 Å to 29.7 Å at the crystal to smectic C phase transition upon heating the sample, Fig. (a) and (b) respectively. This peak shifts position slightly along with the (001) peak due to the smectic layering as the temperature is varied through the smectic and nematic phases. This unexpected peaks could arise from either packing considerations or from impurities in the sample. The ongoing GSAS modeling will show if this is a packing consideration or not. A separation by reverse phase HPLC is planned to look for contaminants.

3) The (001) and (002) reflection from both the smectic layering and the unexplained peak discussed in sections 1) and 2) above are observed to persist in the nematic and into the isotropic phases, see Fig. (d). Such persistence of scattering peaks has been reported in X-ray scattering experiments and is thought to arise from excluded volume effects².

4) Many peaks are observed at small d-spacings. I am attempting to grow a single crystal of this material which will be used to determine the crystal structure by X-ray crystallography. This information will then be used to index the peaks seen in the neutron scattering data.

The newly commissioned 14 degree detector banks which approximately span $3 \text{ Å} < d < 33 \text{ Å}$ were crucial to this investigation. I wish to thank Robert VonDreele for his assistance with this experiment and the GSAS program.

Figure (a) Crystal phase, 67 °C

Figure (b) Smectic C phase, 71 °C

Figure (c) Smectic A phase, 74.9 °C

Figure (d) Nematic phase, 81 °C

References:

- 1) J. Als-Neilsen et al., *Phys. Rev. B*, Vol. 22 No. 1, pp 312-20 (1980).
- 2) W. L. McMillan, *Phys. Rev. A*, Vol. 6 No. 3, pp 936-47 (1972).

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900319			
Title: Strain and Particle Size in Standard Reference Material Aluminas		Report received: <i>(for LANSCE use only)</i> 6/26/91			
Authors and affiliations: R.B. Von Dreele, LANSCE, Los Alamos National Laboratory J. Cline, Mat. Sci. Div., National Institute of Science and Technology					
Experiment report: As part of a program to develop a Standard Reference Material (SRM) alumina with well characterized powder diffraction line shapes, we examined the neutron powder diffraction patterns from four commercially available aluminas using HIPD. Each sample was contained in the standard 3/8" vanadium can and run for 0.5-3hrs. One additional sample consisted of a stack of alumina pellets cut from a hot-pressed disk. In all cases the data collected in the $\pm 153^\circ$ detector banks was subjected to a Rietveld refinement with identical parameter sets. The pellets included parameters for preferred orientation. The results of these refinements (Table 1) are in remarkable agreement with essentially identical structural parameters. The only differences (apart from the preferred orientation) appear in the extinction coefficients with Linde-C showing no extinction and evidently sub micron crystallite sizes. The largest extinction was observed for the hot-pressed pellets with an average crystallite size of $\sim 4\mu\text{m}$. The lattice parameters particularly the c/a ratio show the anisotropic effects of residual stress in that sample.					
Table 1. Refined vaules for SRM candidate aluminas					
Sample	SRM 5257	Linde-C	Alcan	Sumomoto	Pellets
a, Å	4.7546(2)	4.7539(4)	4.7535(3)	4.7532(9)	4.7507(3)
c, Å	12.9784(6)	12.9770(11)	12.9759(9)	12.9752(8)	12.9715(8)
c/a	2.72965	2.72976	2.72976	2.72978	2.73044
Al(z)	0.35232(3)	0.35228(5)	0.35228(4)	0.35232(4)	0.35226(6)
Al(U _{iso})	0.00144(5)	0.00127(10)	0.00106(8)	0.00115(8)	0.00102(9)
O(x)	0.30625(4)	0.30619(6)	0.30615(5)	0.30617(5)	0.30595(5)
O(U _{iso})	0.00244(4)	0.00225(7)	0.00218(6)	0.00214(6)	0.00261(7)
Pref. Ori.	0	0	0	0	1.313(2)
Ext(ave)	2.3(5)	0	7.0(9)	5.0(8)	17.5(10)
$\sigma_1^2(+153)$	50.5(5)	46.4(8)	43.1(7)	45.9(7)	44.2(6)
$\sigma_1^2(-153)$	90.8(8)	85.5(13)	83.0(11)	85.5(11)	85.8(10)
$\sigma_{1e}^2(+153)$	0.6(12)	1.0(19)	-0.6(15)	-1.2(15)	-4.7(20)
$\sigma_{1e}^2(-153)$	4.4(19)	6.2(32)	2.7(2.6)	2.0(26)	-6.7(35)
R _{wp}	3.35	5.34	5.30	5.03	5.34
R _p	2.31	3.50	3.53	3.30	3.98
χ^2	3.409	1.344	1.598	1.651	6.072

Instrument used: <i>(please type)</i> HIPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900316	
Title: Residual Stress in Al ₂ O ₃ /TiC Composites		Report received: <i>(for LANSCE use only)</i> 6/26/91	
Authors and affiliations: R.B. Von Dreele, LANSCE, Los Alamos National Laboratory H. Priesmeyer, GKSS-Geesthacht Institut, Germany			
Experiment report: As a preliminary experiment to determine the possibility of measuring residual stress on HIPD, three hot-pressed samples were examined at room temperature. They were pure Al ₂ O ₃ , pure TiC and a 50/50 composite of the two. They were run for 1.5-2.5hrs and the diffraction data for the $\pm 153^\circ$ detector banks was analysed by Rietveld refinement to extract the lattice parameters and other structural information (Table 1). The differences in the lattice parameters are on the order of 2×10^{-4} and are thus probably due to slight differences in the sample positions for the three runs. However, of potentially more interest is the differences in apparent crystallite size for these materials as reflected in the refined values of the extinction.			
Table 1. Parameters for Al ₂ O ₃ /TiC hot-pressed composites			
Sample	Al ₂ O ₃	TiC	Al ₂ O ₃ /TiC
a, Å	4.7531(3)		4.7548(2)
c, Å	12.9799(8)		12.9848(6)
c/a	2.73083		2.73088
a, Å		4.3207(2)	4.3218(2)
E(Al ₂ O ₃)	0		12.0(10)
E(TiC)		12.0(20)	0
Evidently, the alumina under the particular conditions of hot pressing did not experience significant grain growth unless in the presence of TiC in the composite. On the other hand the composite formation prevents grain growth for TiC.			

Instrument used: <i>(please type)</i> NPD	Local contact: R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 900318
Title: "Neutron Diffraction Study of $\text{Cu}_2\text{Al}_4\text{O}_7$ "		Report received: <i>(for LANSCE use only)</i> 6/6/91
Authors and affiliations: S.J. Marin, Department of Chemistry, Arizona State University M. O'Keeffe, Department of Chemistry, Arizona State University D. Partin, Department of Chemistry, Arizona State University R.B. Von Dreele, Manuel Lujan, Jr. Neutron Scattering Center, Los Alamos National Laboratory		
Experiment report: <p>The refinement of $\text{Cu}_2\text{Al}_4\text{O}_7$ is still in progress. This work is part of a continuing study of the Cu-Al-O system. Three phases in this system are reported to have spinel-type structures. CuAl_2O_4 is a cubic normal spinel. $\text{Cu}_2\text{Al}_4\text{O}_7$ is an oxygen-deficient spinel phase, and CuAl_5O_8 is a tetragonal spinel-related phase.</p> <p>It is believed that the metal atoms in $\text{Cu}_2\text{Al}_4\text{O}_7$ are in the same arrangement as the spinel phase, with a different oxygen framework.</p>

**Neutron Powder
Diffractometer
(NPD)**

Neutron Powder Diffractometer (NPD)

The Neutron Powder Diffractometer (NPD) sample position 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 ($\Delta d/d=0.17\%$) 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	50 - 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

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce Goldstone	Proposal number: <i>(for LANSCE use only)</i> 3307.0
Title: Crystal structure of dickite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, at 10 K		Report received: <i>(for LANSCE use only)</i> 3/5/91
Authors and affiliations: David L. Bish Geology & Geochemistry, EES-1 Earth & Environmental Sciences Division Mail Stop D469 Los Alamos National Laboratory Los Alamos, NM 87545		
Experiment report: <p>Dickite is a relatively common polymorph of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and is isochemical and closely related to the very common clay mineral kaolinite. The "accepted" space group of dickite is Cc, although some infrared spectroscopic data suggest that the space group may be lower. Because dickite forms well-ordered crystals (as opposed to kaolinite, which exhibits considerable layer-stacking disorder and very fine crystallite sizes), its structure has been used as a model for the structures of the kaolin minerals. Much effort has gone into determining the accurate structures of the kaolin minerals, particularly the details of the hydroxyl group orientations and the interlayer bonding.</p> <p>The crystal structure of dickite was originally determined in 1956 by Newnham and Brindley using single-crystal X-ray diffraction data. Since that time, several refinements of the structure, using both X-ray and neutron diffraction data, have been published, all in space group Cc with four crystallographically distinct hydrogen positions (Newnham, 1961; Adams and Hewat, 1981; Sen Gupta et al., 1984; Joswig and Drits, 1986). In spite of the variety of refinements available on well-crystallized materials, considerable uncertainty remains regarding the orientation of the hydroxyl groups that are so important in determining and understanding the details of the interlayer bonding. For example, published O-H bond lengths in dickite range from 0.715 Å to 1.249 Å for the four hydrogens in similar environments, whereas typical accurate refinements of similar materials at room temperature yield O-H bond distances of 0.97 ± 0.2 Å.</p> <p>With the assistance of J. Goldstone in LANSCE, I obtained time-of-flight (TOF) neutron powder diffraction data on the -325-mesh fraction ($<44\mu\text{m}$) of a pure sample of dickite from St. Claire, Pennsylvania. The data were obtained at ~12K, and the Rietveld refinement program GSAS was used to refine the crystal structure, using the non-hydrogen atom positions of Joswig and Drits (1986) as a starting model. Initially, refinement of scale factors and profile and lattice parameters was performed, with the positions of the non-hydrogen atoms fixed and no hydrogen atoms included. Difference-Fourier maps were then calculated in order to locate the missing hydrogen atoms. The Fourier maps consistently indicated the existence of four significant negative regions of density, with other minor negative and positive regions. No significant anisotropy was evident in any of the apparent hydrogen density, unlike the maps obtained for kaolinite using D1A data. The four apparent hydrogen positions were then added to the asymmetric unit, and Rietveld refinement proceeded. Anisotropic profile coefficients and a preferred orientation correction ([001]) were then refined, followed by isotropic temperature factors for groups of similar atoms (all O atoms, all hydroxyl O atoms, all H atoms, all Al atoms, and all Si atoms grouped together, respectively). These</p>		

Experiment report (continued):

parameters were followed by an absorption correction, which apparently did not function properly, probably due to the large absorption cross section of the 3/8" V can of dickite; diffraction may have been occurring only near the outside of the can. Although the sample contained a large amount of hydrogen and would be expected to absorb neutrons to a greater extent than the V can, the refined absorption correction was negative. The correction was refined in subsequent cycles, but it is obvious that problems with its refinement led to inaccurate values for atomic temperature factors, some of which were negative. Soft constraints were implemented and refinement of all atomic positions was then performed. A final set of cycles (overall $R_{wp} = 2.55\%$, reduced $\chi^2 = 1.86$) with anisotropic H atoms did not reveal significant anisotropy. Because of the excellent fit to the data with this structural model, further refinement in a lower space group which would allow >4 independent H positions was not attempted. Furthermore, the lack of significant anisotropy in the H positions does not argue for a lower symmetry.

The resulting non-hydrogen structure in Cc is very similar to those previously published, but the refined H positions differ significantly from literature values (Table 1). In addition, the refined lattice parameters [$a = 5.1496(5)$ Å; $b = 8.9424(9)$ Å; $c = 14.396(2)$ Å; $\beta = 96.484(1)^\circ$] differ from those reported most recently by Joswig and Drits (1986), but refinements using room-temperature X-ray powder diffraction data sets for several different dickite samples show that the parameters reported by Joswig and Drits are in error. O-H distances range from 0.937 to 0.969 Å, Si-O distances vary from 1.607 to 1.623 Å, and Al-O distances extend from 1.887 to 1.957 Å.

Table 1. Positional and isotropic thermal parameters for dickite at 12 K

Atom	x	y	z	U_{iso}
Si(1)	0.0137(4)	0.39959(18)	0.03977(14)	-0.0023(3)
Si(2)	0.9977(4)	0.07079(20)	0.03980(14)	-0.0023(3)
Al(1)	0.9129(5)	0.24900(22)	0.22760(20)	0.0003(3)
Al(2)	0.4123(5)	0.41521(25)	0.22697(21)	0.0003(3)
O(1)	0.9555(3)	0.23596(14)	0.99387(14)	-0.0004(1)
O(2)	0.2583(3)	0.46939(18)	0.99334(15)	-0.0004(1)
O(3)	0.7661(3)	0.50495(17)	0.00911(16)	-0.0004(1)
O(4)	0.0788(3)	0.38779(20)	0.15167(12)	-0.0004(1)
O(5)	0.0056(4)	0.07919(20)	0.15213(12)	-0.0004(1)
OH(1)	0.5827(4)	0.27349(22)	0.15589(17)	0.0007(2)
OH(2)	0.2451(3)	0.27429(23)	0.29764(14)	0.0007(2)
OH(3)	0.2445(4)	0.89128(21)	0.29871(16)	0.0007(2)
OH(4)	0.3189(4)	0.58148(22)	0.29714(14)	0.0007(2)
H(1)	0.4779(6)	0.1867(5)	0.1584(6)	0.0143(4)
H(2)	0.3004(9)	0.2556(4)	0.36320(29)	0.0143(4)
H(3)	0.3237(8)	0.0529(6)	0.8505(4)	0.0143(4)
H(4)	0.7846(9)	0.0826(6)	0.35972(23)	0.0143(4)

References:

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Instrument used: <i>(please type)</i> NPD	Local contact: Joyce A. GoldStone	Proposal number: <i>(for LANSCE use only)</i> 3308
Title: THE DISTORTION OF THE ANTI-PEROVSKITE NITRIDE AsNCa₃.		Report received: <i>(for LANSCE use only)</i> 2/25/91
Authors and affiliations: Ming Y. Chern and F. J. DiSalvo, Chemistry, Cornell, J. B. Parise, ESS, SUNY, Stony Brook., Joyce A. Goldstone, LANSCE.		
Experiment report: <p>The structure of the distorted anti-perovskite nitride AsNCa₃ has been studied both by neutron powder diffraction at 305 K and 15 K and by x-ray powder diffraction at room temperature. AsNCa₃ is distorted to an orthorhombic cell with a and $b \approx \sqrt{2} a'$ and $c \approx 2a'$, where a' is the lattice constant of the ideal undistorted cubic anti-perovskite. The distortion is produced by tilting of octahedra of Ca₆N and results in six short and six long bond distances of the twelve-fold coordinated As atom by Ca atoms. The refined parameters are given in Table 1 and 2.</p> <p>Calcium nitride was initially prepared¹ by heating granular calcium in an N₂ atmosphere at 900°C. A homogeneous, stoichiometric mixture of Ca₃N₂ and As was made up in a dry box; Ca₃N₂ and the product are moisture-sensitive. AsNCa₃ was subsequently prepared by heating a pressed pellet of the mixture under flowing N₂ in an alumina crucible. The furnace was heated at 100°C/hr to 1000°C and held at that temperature for two days. The N₂ gas (99.995%) was pre-purified by passing it through a column of finely divided copper powder at 150°C and then through a column of activated molecular sieves to remove traces of O₂ and H₂O.</p> <p>An estimation of the space group symmetry was made using the observed superlattice reflections, which could be indexed on the basis of an orthorhombic unit cell, and the methodology outlined by Glasser^{2,3}. The distorted structure of the anti-perovskite nitride AsNCa₃ belongs to the the tilt system $a^-a^-c^+$, according to Glazer's classification^{2,3}. For comparison, it will be interesting to solve the structure of the other distorted anti-perovskite, PNCa₃, of the same family.</p>		

Experiment report (continued):

Table 1. Structural parameters at 305 K determined by Rietveld refinement of the neutron powder-diffraction data.

SPACE GROUP: Pbnm

LATTICE CONSTANTS $a=6.7301(2)$, $b=6.7246(2)$, $c=9.5402(2)\text{\AA}$

ATOM	POSITION	x	y	z	$U_{\text{iso}} \times 10^2$
C a(1)	(8d)	0.7211(5)	0.2821(5)	0.0174(2)	1.47
C a(2)	(4c)	0.0310(4)	0.4947(77)	0.2500	1.76
N	(4b)	0.5	0.0	0.0	0.9
As	(4a)	0.0	0.0108(4)	0.25	1.35

Table 2. Structural parameters at 15 K determined by Rietveld refinement of the neutron powder-diffraction data.

LATTICE CONSTANTS: $a=6.7159(2)$, $b=6.7110(2)$, $c=9.5198(2)\text{\AA}$

ATOM	POSITION	x	y	z	$U_{\text{iso}} \times 10^2$
Ca(1)	(8d)	0.7171(3)	0.2821(3)	0.0209(1)	0.54
Ca(2)	(4C)	0.0404(3)	0.4942(4)	0.2500	0.57
N	(4b)	0.5000	0.000	0.0000	0.53
AS	(4a)	0.0000	0.0168(2)	0.2500	0.42

Table 3 Selected interatomic distances ($\text{\AA}$) for AsNCa_3

atoms	305 K	10 K
N-Ca(1)	2.387(4)	2.3975(25)
	2.416(4)	2.4059(25)
N-Ca(2)	2.3944(3)	2.3957(V)
As-Ca(1)	3.0830(23)	3.0602(14)
	3.2649(22)	3.2555(15)
	3.4320(18)	3.3966(13)
	3.7293(18)	3.7868(20)
As- Ca(2)	3.1582(28)	3.0901(21)
	3.261(5)	3.2156(27)
	3.477(5)	3.5173(27)
	3.5754(29)	3.6326(21)

The support of this work by the Office of Naval Research is greatly appreciated.

References:

1. M. Y. Chern, D. A. Vennos and F. J. DiSalvo, to be published.
2. A. M. Glazer, *Acta Crystallogr. B* **28**, 3384 (1972).
3. A. M. Glazer, *Acta Crystallogr. A* **31**, 756 (1975).

Acknowledgements

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce A. Goldstone	Proposal number: <i>(for LANSCE use only)</i> 3309
Title: Neutron Diffraction Study of Alpha, Beta, and Gamma Phases of Neptunium		Report received: <i>(for LANSCE use only)</i> 1/16/91
Authors and affiliations: Joyce A. Goldstone, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 Andrew C. Lawson, MST-5, Los Alamos National Laboratory, Los Alamos, NM 87545 Barbara Cort, NMT-5, Los Alamos National Laboratory, Los Alamos, NM 87545 Elizabeth Foltyn, NMT-9, Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>Neptunium belongs to a small group of actinide elements (Pa, U, Np, Pu) which have multiple and unusual crystal structures between room temperature and their melting points. Neptunium metal exists in three allotropic forms under normal pressure conditions. [1-4] The α-phase is orthorhombic and exists from below room temperature up to 555 K at which point it transforms to the tetragonal β-phase. The transformation from the β-phase to the cubic γ-phase occurs at 830 K, prior to melting at 910 K.</p> <p>Thermal expansion measurements using conventional dilatometry methods[1] with high-purity samples suffered from two experimental problems. First, measurements in the highest temperature phases are unreliable because the sample begins to soften and sag, leading to what is known as "creep" when a pushrod dilatometer is used. Second, the high-purity neptunium metals exhibits a large degree of preferred orientation. The latter has been confirmed by both optical metallography [1] and electron microscopy[5]. Attempts to quench the sample through the phase transition and thereby destroy the preferred orientation have been unsuccessful. Differential thermal analysis (DTA) experiments[6] have indicated a possible fourth allotope of Np. The effect shows up as a sharp shoulder seen on the β-to-γ transition upon heating and as a small, but separate, peaks below the same transition upon cooling.</p> <p>Neutron diffraction data were collected over a temperature range of 300 K to 870 K using a vacuum furnace developed for these experiments. The spread in the temperature was typically less than 2 K. Data were fit using the Rietveld refinement code GSAS[7]. All three phases were observed during the experiment, with data at multiple temperatures obtained for each phase. Lattice and volumetric expansion data were fit using quadratic equation, as linear fits did not give satisfactory results. Table I below gives the thermal expansion at the midpoint of the temperature range for each phase. These measurements represent the first thermal expansion values extracted for the gamma phase of Np. Thermal expansion values for the α phase agree well with the original x-ray measurements[3] and subsequently dilatation measurements[1]. In the β phase, the large anisotropy in thermal expansion between the a and c lattice parameters remains, while the detailed values disagree with the original x-ray results. The volumetric expansion for the β phase is in good agreement with the dilatometric measurement. The isotropic and anisotropic Debye temperatures extracted from the temperature dependence of the thermal displacement are given in Table II.</p> <p>A search for a possible fourth allotope upon cooling from the highest temperature was also conducted. No additional structure was observed from 844 K down to 823 K. Supercooling of the high temperature γ phase down to 828 K was observed.</p>		

Experiment report (continued):

Table I: Thermal Expansion Values for α , β , and γ Neptunium in units of 10^{-6} K^{-1} compared with refs. [1] and [3]

Phase	Temperature Range (K)	Volumetric	a-parameter	b-parameter	c-parameter
alpha	299-526	31.1(1)	27.44(6)	32.20(1)	33.65(1)
	273-550	27.5 [3]	24 [3]	25 [3]	34 [3]
	300-525	27.6(14) [1]			
beta	575-844	63.33(1)	87.1(1)		17.9(5)
	555-700	41 [3]	64 [3]		≈ 0 [3]
	550-850	60.5(22) [1]			
gamma	828-867	62.7(9)	61.7(8)		

Table II: Isotropic and Anisotropic Debye Temperatures

Phase	Atom	Isotropic Θ_D (K)	direction	Anisotropic Θ_D (K)	x	y	z
alpha	Np-1	164(2)	xx	176(5)	1/4	0.21	0.03
			yy	146(3)			
			zz	160(4)			
	Np-2	160(2)	xx	173(4)	1/4	0.84	0.31
			yy	147(3)			
			zz	150(3)			
beta	Np-1	97(2)	xx	94(2)	1/4	1/4	0.4
			zz	107(3)			
	Np-2	92(1)	xx	95(2)	3/4	1/4	0
			zz	100(2)			
	gamma	96(3)			0	0	0

References:

- [1] B. Cort, "Thermal Expansion of Neptunium", J. Less Common Metals 135 (1987) L13.
- [2] W. H. Zachariasen, "Crystal Chemical Studies of the 5f Series of Elements, XVII. The Crystal Structure of Neptunium Metal", Acta Cryst. 5 (1952) 660.
- [3] W. H. Zachariasen, "Crystal Chemical Studies of the 5f Series of Elements, XVII. The Crystal Structure of Neptunium Metal at Elevated Temperatures", Acta Cryst. 5 (1952) 664.
- [4] H. A. C. MacKay, J. S. Naim, and M.B. Waldron, "The Chemistry and Metallurgy of Neptunium", Proceedings of the 2nd Inter. Conf. on Peaceful Uses of Atomic Energy, Geneva, 1958, United Nations, Paper P304, Vol. 28
- [5] K. A. Johnson, unpublished;
- [6] E. Foltyn, unpublished.
- [7] A. C. Larson and R. B. Von Dreele, "Generalized Structure Analysis System", Internal Los Alamos Report, LA-UR 86-748

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce Goldstone	Proposal number: <i>(for LANSCE use only)</i> 3311.0
Title: Determination of hydrogen positions in turquoise using neutron diffraction		Report received: <i>(for LANSCE use only)</i> 1/8/91
Authors and affiliations: George Guthrie and David Bish EES-1 Geology/Geochemistry Los Alamos National Laboratory		
Experiment report: <p>A neutron powder diffraction data set was collected on NPD in June, 1989, using our sample of turquoise $[\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}]$; space group PT, $a = 7.424 \text{ \AA}$, $b = 7.629 \text{ \AA}$, $c = 9.910 \text{ \AA}$, $\alpha = 68.61^\circ$, $\beta = 69.71^\circ$, $\gamma = 65.08^\circ$. Data were collected at 12K for 2 days, though the effective beam time was much less than 2 days. Because of the large hydrogen content of turquoise, we had attempted to deuterate our sample by alternately exposing it to a vacuum (~20 mtorr) and D_2O vapor during the two months prior to the experiment. Our X-ray diffraction and thermogravimetric analysis experiments last spring suggest that some of the hydrogen in turquoise is associated with loosely bound water that can be removed and reintroduced by such a treatment.</p> <p>We have been using GSAS to generate difference-Fourier maps from the LANSCE data. Difference maps were generated using a model consisting of non-hydrogen positions as reported by Cid-Dresdner (1965) and Rietveld-refined instrument-related parameters. Positions of peaks were compared with the positions of oxygens in the structure. Any negative peaks approximately 0.095 nm from an oxygen were assumed to be hydrogen, and positive peaks within 0.095 nm of an oxygen were assumed to be deuterium. When two or more peaks were within 0.095 nm of an oxygen, only the two peaks possessing an angular relationship close to that observed in water were considered. Located Hs and Ds were then entered into the model, and difference maps were recalculated. Using this procedure, positions of 6 negative peaks satisfying the above criteria were located. The remaining 2 sites are apparently partially occupied by both D and H, and hence they produce no large peaks on a difference-Fourier map. Figure 1 shows the neutron data and the pattern calculated from our present model.</p>		

Turquoise, Altar, Chile
(collected at 12K on the -90° bank of NPD)

Figure 1. Neutron powder diffraction pattern for turquoise. Crosses represent data points collected on the 90° detector bank on NPD; upper solid curve represents the pattern calculated from our model that includes 6 of 8 hydrogens in the structure; lower solid curve represents the difference between the observed and calculated data.

We have rehydrogenated the turquoise sample and are scheduled to collect another neutron data set on GPPD at IPNS. With this data set, we hope to confirm the positions of the hydrogens we have located so far and locate the positions of the remaining two hydrogen sites. Once these sites are located, we can use the LANSCE and IPNS data sets to determine partitioning coefficients for D and H on the various sites.

References:

Cid-Dresdner, H. (1965) Determination and refinement of the crystal structure of turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$. *Z. Krist.*, **121**:87-113.

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce Goldstone	Proposal number: <i>(for LANSCE use only)</i> 3318
Title: Structure Solution of Large-Pore Aluminum Phosphates		Report received: <i>(for LANSCE use only)</i> 11/29/90
Authors and affiliations: Abraham Clearfield, Nancy K. McGuire, and Jaime Perez Department of Chemistry, Texas A&M University, College Station TX		
Experiment report: <p>A recently synthesized phase of AlPO_4, referred to as VPI-5, has attracted much interest in the catalyst industry because of the large pores (approximately 12 Å in diameter) which are an integral part of its crystal structure. A crystal structure has been published for VPI-5 ⁽¹⁾ using conventional x-ray powder diffraction data; however, the refinement was quite poor due to particle size and preferred orientation effects. An improved structure refinement was obtained from synchrotron x-ray data ⁽²⁾. The sample used for this refinement had the same overall topology as the published VPI-5 structure, but it underwent a phase change upon heating to 300°C, unlike VPI-5, which is stable to 600°C. Also, this second sample contained both water molecules and residual amine template material from the synthesis procedure. It has been suggested that this thermally unstable form is the $\text{AlPO}_4\text{-H1}$ phase, which had been observed previously only as a component of a multiphase mixture. ⁽³⁾</p> <p>Subsequent improvements in the method of synthesis of aluminum phosphates in our laboratory have produced template-free forms of both the VPI-5 and H1 phases. Several other large pore AlPO_4 phases have been produced as a result of variations in our synthesis procedures. One of these has been identified as $\text{AlPO}_4\text{-8}$. ⁽⁴⁾ This phase can be obtained either as a decomposition product from the heating of H1 or by direct synthesis. A previously unreported phase has been shown to be a hydrated form of $\text{AlPO}_4\text{-8}$, but significant differences in the diffraction patterns of these two phases suggest a change in the structure of $\text{AlPO}_4\text{-8}$ upon hydration.</p> <p>Neutron diffraction scans taken on the NPD were used to supplement diffraction information from both synchrotron and conventional x-ray sources for the following phases:</p> <ul style="list-style-type: none"> VPI-5, dehydrated VPI-5, hydrated with D_2O H1, dehydrated $\text{AlPO}_4\text{-8}$, dehydrated $\text{AlPO}_4\text{-8}$, hydrated with D_2O. 		

Experiment report (continued):

Each of these samples was run at room temperature for approximately 24 hours. The samples were contained in vanadium cylinders, and were loaded under dry helium.

Since the diffraction scans from all of these samples had fairly high incoherent backgrounds, despite our best efforts to deprotonate the samples, none of the neutron scans could be refined independently. However, the neutron diffraction peaks for d-spacings at or below 4 Å provided information on structural details which were not well-resolved by the x-ray scans. Rietveld refinement of the x-ray and neutron datasets is in progress. The program GSAS ⁽⁵⁾ is being used to refine the x-ray and neutron datasets for each phase simultaneously. Since the overall framework for $\text{AlPO}_4\text{-8}$ is still in question, direct methods are being used to obtain an independent structure solution from the raw data prior to Rietveld refinement.

References:

1. P. R. Rudolf, C. E. Crowder, *ZEOLITES*, **10**, 163 (1990).
2. A. Clearfield, N. McGuire, J. Perez, presentation at the American Crystallographic Association 1990 Meeting.
3. F. d'Yvoire, *Bull. Soc. Chim. France* **1961**, 1762.
4. R. M. Dessau, J. L. Schlenker, J. B. Higgins, *ZEOLITES* **10**, 522 (1990).
5. GSAS, A. C. Larson, R. B. VonDreele, GSAS, Los Alamos National Laboratory Report No. LA-UR-86-748 (1987).

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
NPD	Goldstone	3321
Title:		Report received: (for LANSCE use only)
Determination of Structural Changes Induced Upon Heating of $\text{NaBa}_3\text{BiO}_6$.		9/5/90
Authors and affiliations:		
Virginia A. Carlson and Angelica M. Stacy; University of California, Berkeley, CA		
Experiment report:		
<p><u>EXPERIMENT SUMMARY:</u> At 550°C, single crystals of yellow $\text{NaBa}_3\text{BiO}_6$ can be precipitated from a molten $\text{NaOH}/\text{Ba}(\text{OH})_2$ flux. The crystals are isolated from the flux matrix using methanol and the crystal structure of this material was solved using single crystal X-ray diffraction. When the isolated crystals are subsequently heated in air (approximately 200°C), they change from light yellow to black. The color change is consistent with a reduction of the bismuth oxidation state ($\text{Bi}(5s^0) \rightarrow \text{Bi}(5s^1 \text{ or } 5s^2)$). One possible cause of reduction of the bismuth is loss of oxygen. However, temperature programmed desorption studies indicate no loss of oxygen. Thus the transition is hypothesized to involve a structural rearrangement in which an internal oxidation/reduction reaction occurs ($\text{O}_2 \rightarrow \text{O}_2^-$; $\text{Bi}^{5+} \rightarrow \text{Bi}^{3+}/\text{Bi}^{4+}$). Initial experiments showed X-ray powder diffraction spectra of both samples to be virtually identical. This observation was not unexpected as we are hypothesizing the structural rearrangement to involve primarily motion of oxygen atoms (a poor scatterer of X-rays). As oxygen scatters neutrons more effectively than X-rays, we undertook a neutron powder diffraction study of "light" and "dark" $\text{NaBa}_3\text{BiO}_6$.</p> <p><u>RESULTS:</u> Data sets were collected on "light" and "dark" $\text{NaBa}_3\text{BiO}_6$ (neutron beam time approximately 20 hrs. each) on the Neutron Powder Diffractometer (NPD). Both data sets appeared very similar. However, the data set from the "dark" sample contained a number of very small peaks that could not be indexed. Lattice parameters and unit cell composition (previously determined for the light sample from single crystal X-ray diffraction) were input into GSAS for both of the data sets. Variables involved in the refinement included an 8 term background function (Fourier series), scale factor, zero point, DIFA, lattice parameters, atom positions, profile coefficients, anisotropic thermal parameters, and absorption and extinction coefficients. For the data set of the "light" material, the final Rp equaled 0.0289 with a χ^2 value of 1.367.</p>		

Experiment report (continued):

As a result of the extraneous peaks, the refinement of the data set for the "dark" material was noticeably worse with $R_p = 0.0468$ and $\chi^2 = 7.972$. The occupancy of the oxygen atoms was refined but full occupancy was found in both cases.

CONCLUSIONS: $\text{NaBa}_3\text{BiO}_6$ undergoes a large structural change when heated to 200°C . This conclusion is evidenced by the presence of new (small) peaks in the neutron powder diffraction spectrum. The most important result is that the new material is crystalline. Although the sample appeared "dark", only a small proportion of the material had been converted. Thus the structure of the new material could not be determined. Therefore in order to solve the structure of "dark $\text{NaBa}_3\text{BiO}_6$ ", longer conversion times must be used or a more efficient means of converting the material must be determined.

References:

Instrument used: <i>(please type)</i> NPD	Local contact: J. Goldstone R.B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3344
Title: Neutron Powder Diffraction Studies of $(\text{ND}_4^+)_{0.25}(\text{ND}_3)_{0.58}\text{TiS}_2^{0.25-}$ and $\text{Na}^{+0.25}(\text{ND}_3)_{0.75}\text{TiS}_2^{0.25-}$: An Investigation of Intralayer Coulombic Repulsions and their Role in Limiting Lewis-Base Transition-Metal Disulfide Redox Chemistry		Report received: <i>(for LANSCE use only)</i> 3/4/91
Authors and affiliations: <p>G.L. Burr and W.S. Glaunsinger, Department of Chemistry, Arizona State Univ., M.J. McKelvy, Center for Solid State Science, Arizona State University, R.B. Von Dreele and J. Goldstone, LANSCE, Los Alamos National Laboratory.</p>		
Experiment report: <p>Redox-rearrangement reactions are generally believed to accompany a wide range of Lewis-base transition-metal disulfide intercalation processes [1]. The ammoniation of TiS_2 is prototypical of this class of reactions, with redox rearrangement resulting in the co-intercalation of NH_3 and NH_4^+. Interestingly, very long equilibrium times (months) are necessary to asymptotically attain the equilibrium ammonium concentration of 25 mol % for both ammoniated TiS_2 and NbS_2. This suggests an equilibrium $2a \times 2a$ NH_4^+ superstructure forms in order to minimize intralayer Coulombic repulsions. Thus, cation-cation repulsions, as well as the chemical potential of the host, appear to dictate the extent that redox reactions accompany ammonia intercalation [2].</p> <p>The equilibrium intercalate $(\text{ND}_4^+)_{0.25}(\text{ND}_3)_{0.58}\text{TiS}_2^{0.25-}$ was studied by NPD at 300 K in an effort to obtain structural evidence for intralayer ordering. However, it was not possible to cool the sample, in its specially designed container, for further study at 12 K as originally proposed. As a result, the similar solvated-cation intercalate $\text{Na}^{+0.25}(\text{ND}_3)_{0.75}\text{TiS}_2^{0.25-}$ was investigated for structural evidence of $2a \times 2a$ ordering by NPD at 300 K instead.</p> <p>All of the diffraction peaks observed for either data set can be indexed to a simple 3R unit cell without intralayer superstructure. This was also observed during the Rietveld refinement of $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ (space group $R\bar{3}m$), where only short-range ordered $2a \times 2a$ regions are believed present due to large numbers of ND_4^+ and ND_3 vacancies [2,3]. However, both data sets do show regions of diffuse scatter near 3 Å, which were not previously observed for $(\text{ND}_4^+)_{0.22}(\text{ND}_3)_{0.34}\text{TiS}_2^{0.22-}$ [3]. We are presently working toward the solutions of these structures using Rietveld refinement and evaluating the cause of the observed diffuse scatter and its possible relationship to intercalant ordering. The data sets from the 90° detector bank are shown below for $(\text{ND}_4^+)_{0.25}(\text{ND}_3)_{0.58}\text{TiS}_2^{0.25-}$ and $\text{Na}^{+0.25}(\text{ND}_3)_{0.75}\text{TiS}_2^{0.25-}$.</p>		

Experiment report (continued):

References:

- [1] M.J. McKelvy and W.S. Glaunsinger, Ann. Rev. Phys. Chem. 41 (1990) 497-523.
- [2] M.J. McKelvy, J.M. Dunn, V.G. Young, Jr. and W.S. Glaunsinger, Solid State Ionics 32/33 (1989) 174-82.
- [3] V.G. Young, Jr., M.J. McKelvy, W.S. Glaunsinger and R.B. Von Dreele, Solid State Ionics 26 (1988) 47-54.

Instrument used: <i>(please type)</i> NPD	Local contact: Dr. Allen Larson	Proposal number: <i>(for LANSCE use only)</i> 3357
Title: Experimental valence densities of α -quartz structures		Report received: <i>(for LANSCE use only)</i> 6/25/91
Authors and affiliations: R.E. Barton and B.E. Robertson, Dept. of Physics, University of Regina		
Experiment report: <p>Neutron powder diffraction data were collected with an as-milled and an annealed sample of quartz, both taken from the same boule. The data were collected at various temperatures, as listed in Table 1, to 130000 t-zeros. The data were collected in order to improve the lattice constants and atomic parameters which are needed to very high accuracy in order to accurately calculate the electro-physical properties of Quartz. The data were analyzed both with and without the primary extinction correction in the GSAS package.</p> <p>The lattice constants, atomic parameters and R-values from the refinement for each temperature are given in Table 1. The R-values are too large for high accuracy calculations.</p> <p>The better R values at 350K and 295K resulted from longer data collection times. The 35K and 210K lattice constants do not follow the smooth second order curve shown by the other as-milled data, but have much larger values, such as would be expected at much higher temperatures. However, in each case the temperature indicated by the two parameters is not the same. The set of lattice constants for the annealed sample deviate only slightly from the trend of the as-milled sample. However this trend is significantly lower than the values reported by Lager, Jorgensen and Rotella(1).</p> <p>Most of the histograms show one or more reflections with excess intensity. The four histograms of a given run do not show excess intensity in the same reflections nor do the histograms from different temperatures. The large R-values are probably related to this problem. Attempts to solve this problem by refining the preferred orientation parameter lead to poorer agreement factors and have not removed the problem. Refinement of the primary extinction coefficient slightly improved the agreement factor and systematically increased the lattice parameters and decreased the atomic parameters by statistically insignificant amounts.</p> <p>To clarify the situation at 35K and 210K it will be necessary to collect new data. In order to improve the accuracy of bond angles and distances the excess intensities will need to be explained. The possibility of a shock induced phase change (handness) during milling is being considered, unsuccessfully to date. New data, preferably with longer collection times, will need to be collected.</p>		

TABLE 1
Temperature Lattice Constants

Temperature Lattice Constants			Atomic Parameters				R-values
(K)	a (Å)	c (Å)	Si x	x	O y	z	Rp
as-milled							
15	4.9005(2)	5.3979(2)	.46748(14)	.41249(10)	.27096(8)	.21728(6)	.057
35	4.9014(2)	5.3988(2)	.46722(12)	.41232(9)	.27076(8)	.21726(6)	.060
78	4.9016(2)	5.3984(2)	.46755(15)	.41228(11)	.27052(10)	.21715(7)	.072
125	4.9027(2)	5.3987(2)	.46813(14)	.41260(10)	.27001(9)	.21667(7)	.064
210	4.9112(2)	5.4056(2)	.46900(14)	.41275(11)	.26835(10)	.21571(7)	.062
295	4.9121(2)	5.4039(3)	.46972(16)	.41307(13)	.26677(11)	.21444(8)	.064
350	4.9157(2)	5.4062(2)	.47036(13)	.41364(11)	.26577(9)	.21378(7)	.047
annealed							
15	4.9011(2)	5.3984(2)	.46835(12)	.41221(8)	.27100(7)	.21732(6)	.061
125	4.9031(2)	5.3990(2)	.46880(12)	.41254(9)	.27038(8)	.21666(6)	.061
295	4.9118(2)	5.4036(2)	.47034(11)	.41339(9)	.26777(8)	.21448(5)	.046

References:

- (1) J. Appl. Phys. 53 (6751 - 6756), 1982

Instrument used: <i>(please type)</i> NPD	Local contact: Angus Lawson, MST-5, MS G730	Proposal number: <i>(for LANSCE use only)</i> 3376
Title: Residual Strain Measurement From an Aluminum Matrix/ Silicon-Carbide Whisker Composite		Report received: <i>(for LANSCE use only)</i> 1/91
Authors and affiliations: Gary Povirk, Brown University, Div. of Engr., Box D, Providence, RI 02912 Alan Needleman, Brown University, Div. of Engr., Box D, Providence, RI 02912 Steven Nutt, Brown University, Div. of Engr., Box D, Providence, RI 02912 Stuart MacEwen, ALCAN International Ltd., P.O. Box 8499, Kingston, Ontario K7L 5L9 Andrew Geltmacher, Pennsylvania State University, University Park, PA 16802 Mark Bourke, Los Alamos, LANSCE, MS H805 Joyce Goldstone, Los Alamos, LANSCE, MS H805 Andrew Lawson, Los Alamos, MST-5, MS G730 Michael Stout, Los Alamos, MST-5, MS G730 Manuel Lovato, Los Alamos, MST-5, MS G730		
Experiment report: <p>Thermally induced residual stresses are inherent in Al/SiC reinforced composites due to the mismatch in thermal expansion of aluminum and silicon carbide. The stresses that develop when cooling the material from its processing temperature could potentially have several consequences. For example, Christman and Suresh [1] found that the presence of residual stresses and resulting high dislocation density in the matrix effects the microstructural development of the aluminum alloy. Residual stresses can also be introduced by plastic deformation of the composite since the hard SiC particles promote nonhomogeneous flow. The object of our investigation was to measure average residual elastic strains by neutron diffraction in Al/SiC composites that had been subjected to different thermal and mechanical histories and to compare the results with model predictions.</p> <p>We ran experiments at the Los Alamos Neutron Scattering Center (LANSCE) to determine bulk residual strains of both constituents in Al/SiC composites, after the material had been subjected a rapid quench and different levels of uniaxial deformation. The specimens included 15 v% SiC whisker and 20 v% SiC particle reinforced composites. Neutron diffraction experiments were also conducted on the unreinforced matrix alloy and on SiC particles and whiskers for use as stress-free references. In addition, continuum-based finite element (FEM) calculations were performed to model the 15 v% SiC whisker-reinforced composite using the methodology proposed in [2]. We assumed that the constituents were elastically isotropic to calculate the predicted levels of residual strains.</p> <p>Preliminary graphs of experimental (measured at LANSCE) and computed bulk residual elastic strains plotted vs. macroscopic plastic strain (overall final state of the composite) are shown for the whisker-reinforced material in Figures 1-3. Although there is considerable scatter in some of the experimental data, the agreement between the measured and predicted values is nonetheless quite remarkable. Refinement of the data reduction will in all probability remove some of the spurious points observed on the graphs. The large difference in measured and predicted values</p>		

Experiment report (continued):

of axial residual elastic strain in the SiC whiskers could be due in part to the assumption of isotropic elasticity in the computations. Another interesting feature of the graphs is the apparent reduction of residual strain in the fractured specimen (i.e., the specimen with maximum plastic strain). One can speculate that the onset of damage serves to reduce the residual strains in a fractured composite.

Figure 1 Calculated and measured residual axial elastic strain in the aluminum matrix vs. macroscopic plastic strain in the composite.

Further data reduction and refinement and more calculations are needed to get a clearer picture of the residual strain state in Al/SiC composites, although the preliminary results reported here are certainly encouraging. These experiments have provided an initial verification of the continuum-based FEM model used to predict microstructural-level residual stresses. The calculation procedure can now be applied to other material systems with a higher level of confidence.

Figure 2 Calculated and measured residual radial elastic strain in the aluminum matrix vs. the macroscopic plastic strain in the composite.

Figure 3 Calculated and measured residual axial elastic strain in the SiC whiskers vs. the macroscopic plastic strain in the composite.

References:

- [1] T. Christman and S. Suresh, *Mat. Sci. Eng.*, (1989) 49.
- [2] G.L. Povirk, A. Needleman, and S.R. Nutt, *Mat. Sci. Eng.*, (1990) 129.

Instrument used: <i>phases 2000</i> NPD, HIPD	Local contact: Robert Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 5387
Title: The structures of some intermediate binary rare earth oxides		Report received: <i>(for LANSCE use only)</i> 3/1/91
Authors and affiliations: Jie Zhang Dept of Chemistry, Arizona State University LeRoy Eyring Dept of Chemistry, Arizona State University Robert Von Dreele Los Alamos National Laboratory		
Experiment report: The 1990 runs at LANSCE provided diffraction information on three compounds: Pr_9O_{16} (high-temperature form), $\text{Pr}_{10}\text{O}_{18}$, and $\text{Pr}_{24}\text{O}_{44}$. These oxides were prepared at Arizona State University by suitable conditioning and annealing in appropriate oxygen atmospheres to fix the desired compositions. Diffraction data were collected from Pr_9O_{16} and $\text{Pr}_{24}\text{O}_{44}$, run on NPD. Diffraction data were collected from all three compounds on HIPD. Subsequent structural analysis were conducted utilizing Rietveld refinement supported by the program package GSAS, as described below.. The Rietveld refinement on a sample of the zeta praseodymium oxide, Pr_9O_{16} ($P\bar{1}$, $Z=1$), was successful. With four banks of data and 107 variables, a structural solution of satisfactory quality was obtained, as indicated by the low values of R/R_w (3.54/5.00%) and reduced χ^2 (1.262). The resulting histograms showed good agreement between the calculated and the observed spectra. Furthermore, the refined structure is reasonable in terms of distances and charge distribution. The refined structure clearly indicated that this intermediate oxide contains oxygen vacancy pairs in the parent fluorite matrix, similar to that observed in the iota phase, Pr_7O_{12} . This structure model is consistent with the high resolution electron microscopy studies [1], and supports the hypothesis that the "Bevan clusters" are the basic building blocks of the $\text{R}_n\text{O}_{2n-2}$ series. The attempts to fit the above model to data sets collected for two other Pr_9O_{16} samples that were annealed at higher temperatures did not refine satisfactorily. This implies that the samples might have a different structure or contain a second phase. Further investigation is necessary to reveal the structures of these samples and to verify the existence of the high- and low-temperature forms of Pr_9O_{16} which have been suggested by X-ray powder diffraction [2].		

Experiment report (continued):

The structure of $Tb_{11}O_{20}$ is currently under study. While the refinements provided evidence in favor of one of the three structurally acceptable models, further persistent studies are required to provide the detailed features of the structure.

Efforts were also made to determine the structure of the beta praseodymium oxide, $Pr_{12}O_{22}$. Although a probable model has been obtained via high resolution electron microscopy [3] application of the Rietveld refinement on this model has not given satisfactory results. The difficulties might arise from the large number of variables that result from the size and the low symmetry of the unit cell ($Z=2$, $P\bar{1}$) which are characteristic of these systems. Possible contaminations from minor phases may have further complicated the problem.

References:

1. R.T. Tuenge and L. Eyring, J. Solid State Chem. 29, 165-179 (1979).
2. J.O. Sawyer, B.G. Hyde and L. Eyring, Bull. Soc. Chim. Fr. 1190-1199 (1965).
3. E. Schweda, D.J.M. Bevan and L. Eyring, J. Solid State Chem., 90, 109-126 (1991).

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce Goldstone	Proposal number: <i>(for LANSCE use only)</i> 3394
Title: Residual strain abatement by vibrational stress relief of weldments		Report received: <i>(for LANSCE use only)</i>
Authors and affiliations: Joyce Goldstone , LANSCE, MS H805 Mark Bourke, LANSCE MS H805 Steve Spooner, Oak Ridge National Laboratory S David, Oak Ridge National Laboratory		
Experiment report: <p>The purpose of the experiment was to assess the effectiveness of vibratory stress relief in reducing the residual stresses near welds. Two multipass welds were fabricated in 12" by 12" by 1" austenitic steel plates one of which was subsequently stress relieved. Strong texture changes were known to occur in the weld metal and heat affected zones because of epitaxial growth of crystals from the melt with <100> directions along lines of heat flow from the weld. Vibratory stress relief is believed to offer an economical alternative to heat treatments, requiring less power and with less likelihood of changing the microstructure. The way this is achieved is not clear and by comparing a stress-relieved with a standard weld we hoped to determine the degree of relief and to elucidate the mechanism.</p> <p>The measurements in this program were started during the 1990 beam cycle but due to poor beam production only about 40% of the time allocated on the NPD was available for experiments. Nevertheless a limited examination and comparison of the through-thickness variation of strain was made in the weld metal. As expected the preferred orientation varied considerably at different positions. One unexpected feature is shown in figure 1 where doublets are clearly visible in the weld metal of the stress relieved specimen. This was unexpected and may be associated with a dramatic localized strain but is more probably due to contamination of the weld metal.</p> <p>The preliminary measurements have shown that studies of strain variation in specimens containing strong and varied texture are particularly suited to a pulsed neutron source where all the lattice collections are collected simultaneously for a single scattering geometry. This is particularly true in a weld where the intensity of individual Bragg reflections sometimes changes dramatically when the sampling volume is moved by only a few millimeters. At a steady state source using monochromatic neutrons it would prove difficult to employ a single reflection throughout the material. Thus changes in wavelength and/or orientation of the specimen would be necessary to obtain other lattice reflections while maintaining the scattering vector correctly aligned relative to the specimen.</p> <p>Preliminary analysis of the strain in the material has so far been limited to individual lattice reflections because the preferred orientation was too severe to extract Rietveld refinements from the data. By using measurements on "stress free" extracts of the weld metal we have calculated the strain variation through the thickness of the weld in the case of the un-stress relieved specimen (the stress relieved specimen showed doublet behavior and the data have not yet been analyzed). An example of the strain variation for several reflections is given in figure 2. The errors on the data are typically $\pm 100\mu\text{strain}$. The strain range suggests a possible stress variation of several hundred MPa although without more comprehensive measurements this is speculative.</p> <p>The analysis of the data is continuing.</p>		

Experiment report (continued):

S.S WELD RS-2, T=20, INC=4MM SLIT, EX =4MM 45 DEG BOTH 8DST
BANK NO. - 4 TWO-THETA - -90.00 OBSERVED PROFILE

Figure 1

Figure 1

Instrument used: (please type) NPD	Local contact: Joyce Goldstone	Proposal number: (for LANSCE use only) 3402
Title: Structural Studies on Alkali Metal-Niobium/Tantalum Phosphate Non-Linear Optical Materials.		Report received: (for LANSCE use only) 6/4/91
Authors and affiliations: William T. A. Harrison, Cheryl S. Liang, Thurman E. Gier and Galen D. Stucky. Department of Chemistry, University of California, Santa Barbara, CA 93106-9510		
Experiment report: <p>The newly-discovered¹ family of alkali metal-niobium/tantalum phosphates, general formula: $M(Nb,Ta)_2PO_8$ ($M = Li, Na, K, Rb, NH_4$) have a novel open framework structure consisting of a network of vertex sharing octahedra (Nb,TaO_6) and phosphate tetrahedra, enclosing large cavities, interconnected <i>via</i> 8-ring windows. Zeolitic cation exchange is possible, and the acentric crystal structure (space group $R\bar{3}2$) shows a large SHG coefficient relative to quartz. Conventional X-ray techniques have proved inconclusive in locating the guest cations, and time-of-flight neutron data were collected to determine lithium and potassium atomic positions. These species were located from difference Fourier syntheses, following framework-atom and profile-parameter refinement. Lithium atom coordination is trigonal pyramidal and the potassium atom is surrounded by seven oxygen atoms. Excellent Rietveld profile fits (<i>vide infra</i>) resulted.</p> <p>These high quality crystallographic data are being used to correlate optical, NMR and other data with the structural model for this new family of phases.</p> <p>1) Liang, Harrison, Eddy, Gier and Stucky. <i>Inorg Chem.</i>, submitted.</p>		

K(2/3)L1(1/3)TA2P08 LIANG/HARRISON

BANK 1, 2-THETA 148.0, L-S CYCLE 44 OBSD. AND DIFF. PROFILES

K2/3L11/3NB2P08 CSL/WTAH

BANK 4, 2-THETA -90.0, L-S CYCLE 106 OBSD. AND DIFF. PROFILES

Instrument used: <i>(please type)</i> Neutron Powder Diffractometer (NPD)	Local contact: Dr. Bob Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3411.0
Title: Low-Temperature Study of Lithium Nitride Deuteride Li ₄ ND		Report received: <i>(for LANSCE use only)</i> 1/2/91
Authors and affiliations: Nathaniel E. Brese and Michael O'Keeffe Department of Chemistry Arizona State University Tempe, AZ 85287-1604		
Experiment report: <p>The preparation of Li₄ND was reported by Brice, Motte, and Aubry, and a Debye-Scherrer photograph was indexed on a large tetragonal cell. Further, they suggested that the material likely crystallizes on a superstructure of anti-fluorite (CaF₂). McMillan and O'Keeffe proposed that Li₄ND may actually be (Li₄N)⁺D⁻, and therefore could crystallize with a superstructure of rocksalt or sphalerite, for example.</p> <p>Unfortunately, the neutron diffraction data exhibit broad Bragg peaks. The cell proposed by Brice does not satisfactorily index all the profile peaks, and our attempts to derive other unit cells have failed. None of the diffraction peaks match those calculated for starting materials (Li₃N and LiD) or likely side reactions (Li₂ND, LiND₂, Li₂O, Li₂O₂, LiOH), although certain similarities are noticeable.</p>		

Experiment report (continued):

LI4ND AT 16K

BANK NO. = 1 TWO-THETA = 148.00

OBSERVED PROFILE

References:

Instrument used: <i>(please type)</i> Neutron Powder Diffractionmeter (NPD)	Local contact: Dr. Bob Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3411.1
Title: Low-Temperature Study of Tantalum Nitride Ta ₃ N ₅		Report received: <i>(for LANSCE use only)</i> 1/2/91
<p>Authors and affiliations:</p> <p>Nathaniel E. Brese and Michael O'Keeffe Department of Chemistry Arizona State University Tempe, AZ 85287-1604</p>		
<p>Experiment report:</p> <p>The structure of Ta₃N₅ was reported in the spacegroups <i>C2/m</i> and <i>Cmcm</i>, although the material is reportedly tetragonal. Curiously short Ta-Ta distances also prompted our study of its structure.</p> <p>Neutron diffraction data confirmed the short Ta-Ta distances. If the material is truly monoclinic, it is too close to orthorhombic to tell; the model refined in <i>C2/m</i> to within a few standard deviations of that refined in <i>Cmcm</i>. A manuscript for publication in <i>Acta Crystallographica</i> is being prepared; the abstract is given below.</p> <p>$M_r = 612.88$, orthorhombic, <i>Cmcm</i>, $a = 3.8862(1) \text{ \AA}$, $b = 10.2119(2) \text{ \AA}$, $c = 10.2624(3) \text{ \AA}$, $V = 407.27(3) \text{ \AA}^3$, $D_x = 9.99 \text{ g cm}^{-3}$, neutron time-of-flight, Rietveld refinement (GSAS), wR_p, R_p, reduced $\chi^2 = 0.061, 0.043, 4.21$ for data collected at 16K. Ta₃N₅ crystallizes with the pseudobrookite (Fe₂TiO₅) structure. Irregular TaN₆ octahedra share edges and corners.</p>		

Experiment report (continued):

Table I. Structure of Ta₃N₅ at 16K^a

Atom	Site	x	y	z	100U _{eqv}
Ta(1)	4c	0	0.1971(1)	1/4	0.56
Ta(2)	8f	0	0.13455(7)	0.55905(7)	0.60
N(3)	4c	0	0.76322(7)	1/4	0.85
N(4)	8f	0	0.04700(6)	0.11949(5)	1.00
N(5)	8f	0	0.30861(6)	0.07378(5)	0.83

^aSpacegroup Cmc₂m, a = 3.88618(9), b = 10.2119(2), c = 10.2624(3). U_{eqv} is defined as 1/3 the trace of the anisotropic temperature coefficients.

Table II. Anisotropic Temperature Factors for Ta₃N₅ at 16K^a

Atom	100U ₁₁	100U ₂₂	100U ₃₃	100U ₂₃
Ta(1)	0.48(3)	0.83(3)	0.37(3)	0
Ta(2)	0.37(2)	0.75(2)	0.69(3)	0.01(2)
N(3)	0.80(3)	0.86(3)	0.88(3)	0
N(4)	1.36(2)	0.81(2)	0.83(2)	-0.08(2)
N(5)	0.70(2)	0.83(2)	0.95(2)	0.12(2)

$$^aU_{12} = U_{13} = 0$$

References:

Instrument used: <i>(please type)</i> Neutron Powder Diffractometer (NPD)	Local contact: Dr. Bob Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3411.2
Title: Low-Temperature Study of Praseodymium Oxides		Report received: <i>(for LANSCE use only)</i> 1/2/91
Authors and affiliations: Nathaniel E. Brese and Michael O'Keeffe Department of Chemistry Arizona State University Tempe, AZ 85287-1604		
Experiment report: <p>We are interested in modeling metal-metal repulsions in crystal structures. Pr_2O_3 can crystallize in two different, simple structures. A-Pr_2O_3 forms with the hexagonal La_2O_3 structure, while C-Pr_2O_3 crystallizes with the bixbyite (Mn_2O_3) one. Accurate crystal structures of A- and C-type Pr_2O_3 will provide suitable data for modeling repulsions.</p> <p>We collected data on A-Pr_2O_3; its refinement was straightforward, and the results are tabulated below. C-Pr_2O_3 has been synthesized, and we hope to run it this summer. This work is in collaboration with Prof. Leroy Eyring at Arizona State University.</p>		

Experiment report (continued):TABLE I. Positional Parameters^a for A-Pr₂O₃ at 17 K.

Atom	Site	x	y	z	100U _{eqv} ^b
Pr	2d	1/3	2/3	0.245422(9) [0.2450(4)]	0.59 1.34]
O(1)	2d	2/3	1/3	0.35182(6) [0.364(1)]	0.83 1.56]
O(2)	1a	0	0.0	0	0.95 [1.14]

^aSpace group *P*-3*m*1. This study: *a* = 3.85080(5) Å, *c* = 5.99259(8) Å; Single-crystal study by Wolf and Hoppe at room temperature in brackets (1): *a* = 3.8577(3) Å, *c* = 6.0120(6) Å.

^bU_{eqv} is defined as 1/3 the trace of the matrix of anisotropic coefficients.

Table II. Anisotropic Thermal Parameters for A-Pr₂O₃ at 17 K^a

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pr	71(1) 116(5)	71(1) 116(5)	68(2) 171(8)	36(1) 58(3)	0 0	0 0
O(1)	92(1) 137(55)	92(1) 137(55)	111(2) 194(73)	46(1) 68(27)	0 0	0 0
O(2)	112(2) 121(64)	112(2) 121(64)	116(3) 101(75)	56(1) 61(32)	0 0	0 0

^aAll values to be multiplied by 10⁻⁴ Å². The lower numbers are those determined from the room-temperature study by Wolf and Hoppe(1).

References:

1. R. Wolf and R. Hoppe, Z. Anorg. Allg. Chem. **529** (1985) 61-64.

Instrument used: <i>epicard</i>	Local contact: Dr. Joyce Goldstone	Proposal number: (for LANSCE use only) 3420.0
Title: Neutron diffraction measurements of the macroscopic stress field in compacted iron components.		Report received: (for LANSCE use only) 1/30/91
Authors and affiliations:		
Prof. Stuart B. Brown	Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, Massachusetts 02139	
Dr. T. M. Holden	Chalk River Nuclear Laboratories Chalk River, Ontario Canada K0J 1J0	
Experiment report:		
<p>The results from our residual strain measurements on powder compacts were both encouraging and frustrating. Although we had scheduled one week of beam time to perform the residual stress measurements, difficulties with the beam permitted us only approximately one-and-one-half days of time. The results of these preliminary experiments were very encouraging. Because of the small amount of available beam time, we were only able to measure radial, axial and hoop strains in one cylindrical compact at a few locations.</p> <p>The residual strains measured were of the approximate magnitude and sign expected, although one specimen and one set of measurements were insufficient to demonstrate that the strains were correct. The measurements suggested a radial variation in strain state in the specimen middle section, varying from compressive radial strains in the center to zero at the edge, with a maximum magnitude of approximately 2 microstrain. Our simulation predicts the same gradient in strain state, with a maximum strain on the order of 1 microstrain. The measurements were also performed on the specimen with the lowest expected residual strains, so the other compacts we intended to examine could have provided strong validation of our initial measurements.</p> <p>Nevertheless, these results are particularly exciting. Many net shape fabrication technologies use powder compaction to form components. Residual stresses, particularly tensile stresses, are one of the major limits to the use of compacted components. These measurements represented the first residual strain (and therefore stress) characterizations ever performed on metal compacts. The resulting data is critical for the calibration and validation of constitutive models for compaction. The measurement of residual stresses may provide the information necessary to arbitrate among the plethora of competing models now promoted within the powder constitutive behavior literature.</p>		

Experiment report *(continued)*:

Given the very promising, albeit preliminary, results of the initial experiments, it is important to complete our experimental program. We have three standard specimen sizes to test. We also need to perform experiments under better calibration, since uncertainties in the initial calibration affected the absolute values, although not the trends, in the data.

References:

1. S. B. Brown and G. G. A. Weber, Modern Developments in Powder Metallurgy, 18-21, 465, (1988).

Instrument used: <i>(please type)</i> NPD	Local contact: R. B. Von Dreele	Proposal number: <i>(for LANSCE use only)</i> 3436
Title: Neutron Powder Diffraction Study of SrCuO ₂		Report received: <i>(for LANSCE use only)</i> 5/31/91

Authors and affiliations:

D. E. Partin and M. O'Keeffe
Department of Chemistry
Arizona State University
Tempe, Az 85287

Experiment report:

SrCuO₂ was synthesized and the structure refined from time-of-flight neutron powder diffraction data.

	x	y	z	u11	u22	u33
Sr	0	0.33091(2)	1/4	0.011	0.007	0.007
Cu	0	0.06102(2)	1/4	0.013	0.006	0.004
O	0	0.94443(3)	1/4	0.018	0.008	0.005
O	0	0.17866(3)	1/4	0.014	0.007	0.008

space group: Cmcn a=3.57002(2), b=16.32268(8), c=3.91100(2)

wRp=4.17, Rp=2.97, and $\chi^2=2.57$

SRCUO2 LAT.POS.ANI.PRO.PRE.ABS
BANK 4, 2-THETA -90 0, L-S CYCLE 89 OBSD AND DIFF PROFILES

Experiment report *(continued)*:

Drawing of the crystal structure of SrCuO₂

References:

A.C.Larson and R.B.Von Dreele, "GSAS-General Structure Analysis System",
LAUR 86-748, Los Alamos National Laboratory Report.

Instrument used: (please type) NPD	Local contact: J. A. Goldstone	Proposal number: (for LANSCE use only) 100018
Title: DEBYE-WALLER FACTORS of δ -PHASE $\text{Pu}_{0.95}\text{Al}_{0.05}$ BETWEEN 15 and 900 K		Report received: (for LANSCE use only) 12-7-90
Authors and affiliations: <p style="margin-left: 40px;">A. C. Lawson and J. Vaninetti, MST-5 J. A. Goldstone, LANSCE R. I. Sheldon, NMT-9 B. Cort, NMT-5</p>		
Experiment report: <p>During our ongoing studies of Debye-Waller factors of actinide elements and alloys, a curious discrepancy had emerged: the Debye-Waller temperature of δ-Pu metal measured at 603-673 K was 70(4) K, while that of δ-$\text{Pu}_{0.95}\text{Al}_{0.05}$ measured in the range 15-280 K was 113(1) K. We therefore decided to extend the measurement of the alloy to 900 K. Neutron powder diffraction data were collected at 18 temperatures on the Neutron Powder Diffractometer (NPD) at LANSCE using a specially designed furnace. Data were taken on repeated heating and cooling cycles, and Fig. 1 shows the result. The figure includes low-temperature data taken in 1987 on the High Intensity Powder Diffractometer (HIPD). The break in the curve at 280 K is the result instrumental differences in the diffractometers and is inconsequential for the following analysis. Near the highest temperature, the alloy has passed into the $\delta+\epsilon$ region of the phase diagram. Between 15 and 710 K, the data of Fig. 1 shows significant positive curvature. We decided to account for this by ascribing a linear temperature dependence to the Debye-Waller temperature.</p> <p>The results are shown in Fig. 2. The decrease of the Debye-Waller temperature from 125 to 95 K with temperature indicates a progressive elastic softening of the alloy as it is heated. This softening brings the Debye-Waller temperatures of pure and alloy δ-Pu into much better agreement.</p> <p>Fig. 1 also shows a distinct break at 710 K. We did not find any structural change at this temperature. 710 K is close to the stability range (725-753 K) for the body-centered tetragonal δ'-phase of pure plutonium. The latter phase is not stable at 5% aluminum, but we speculate that the observed break signifies an electronic transition that is ultimately responsible for the existence of the δ'-phase in pure plutonium.</p>		

Experiment report (continued):

Fig. 1. Mean-square thermal displacement versus temperature for $\delta\text{-Pu}_{0.95}\text{Al}_{0.05}$.

Fig. 2. Debye-Waller temperature versus temperature for $\delta\text{-Pu}_{0.95}\text{Al}_{0.05}$.

Instrument used: <i>(please type)</i> NPD	Local contact: Joyce A. Goldstone	Proposal number: <i>(for LANSCE use only)</i> 900101
Title: Neutron Diffraction Study of Scandium Deuteride at Low Temperatures		Report received: <i>(for LANSCE use only)</i> 1/16/91
Authors and affiliations: J. A. Goldstone, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 A. C. Lawson, MST-5, Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>Scandium hydride behaves in a similar manner as the rare-earth dihydrides. The structure is the classic CaF_2 ($\text{Fm}\bar{3}\text{m}$) except that loading up to and beyond the dihydride composition under normal pressure conditions is not possible. In the $\text{Fm}\bar{3}\text{m}$ structure, there are two tetrahedral sites and one octahedral site per metal atom available for hydrogen occupancy. Only the tetrahedral site is observed to be occupied in scandium hydrides. Anomalous behavior has been reported in acoustic velocity measurements suggesting a phase transition around 240 K in $\text{ScH}_{1.99}$ [1]. ESR and x-ray data on $\text{Sc}_{0.995}\text{Gd}_{0.005}\text{H}_{1.98}$ indicate a possible phase transition below 140 K [2]. Since x-ray diffraction studies show no change in the scandium position nor the crystal structure, a neutron diffraction investigation was undertaken to examine possible changes in the position of the deuterium and/or ordering of the deuterium on the tetrahedral site.</p> <p>During the 1989 run cycles, neutron diffraction patterns were collected for a sample of $\text{ScD}_{1.98}$ over the temperature range of 15 to 305 K.[4] During this time, insufficient data were collected at the lowest temperatures, so data were collected from 25 K to 145 K in 20 K steps during the 1990 run cycles. In addition, a x-ray scan at 302 K was completed using the LANSCE Scintag XDS2000. Data were fit using the Rietveld refinement code GSAS.[3] All diffraction data were successfully fit with using the space group $\text{Fm}\bar{3}\text{m}$ with scandium occupying the (0,0,0) position and the deuterium in the (1/4,1/4,1/4) position. No evidence of superlattice peaks arising from an ordering of the deuterium atoms was found. In addition, displacement of the deuterium off the high symmetry site to a more general (x,x,x) position did not improve the fit to the data. Figure 1 shows a partial neutron diffraction pattern of $\text{ScD}_{1.98}$ at 135 K. Figure 2 shows the lattice parameter versus temperature for all the runs. Even with the finer temperature steps, no indication of an anomalous change is observed over this temperature range. In addition to the lattice parameter data, the temperature dependence of the thermal displacement can be extracted from the fits. The slope of a Debye model fit to the thermal displacement data is the Debye temperature of the atom. The value obtained for scandium is 447.3(7) K and for deuterium 1649(5). The ratio of the Debye temperatures should be equal to the square root of the masses of the atoms; the mass ratio is 4.7 while the Debye temperature ratio is 3.7, so reasonable agreement exists.</p> <p>The absence of a contraction of the lattice parameter at low temperatures in this $\text{ScD}_{1.98}$ sample does not rule out the possibility of a contraction of the lattice parameter in the scandium hydrides; this effect may be strongly isotope dependent. It may be worthwhile to investigate scandium hydride using neutron diffraction, a considerably more tedious task.</p>		

Experiment report (continued):

This figure shows a partial neutron diffraction pattern of ScD_2 at 135K; the +s are the observed data, the line through the data is the Rietveld fit, the lower curve is the difference between the observed data and the fit, and the vertical ticks mark the positions of allowed reflections for the space group.

This figure shows the lattice parameter versus temperature for all data collected on $\text{ScD}_{1.98}$. The error bars are approximately the size of the data points

References:

- [1] A. G. Beattie, J. Appl. Phys. 43 (1972) 3219.
- [2] E. L. Venturini and B. Morosin, Physics Letters 61A (1977) 326.
- [3] A. C. Larson and R. B. Von Dreele, "Generalized Structure Analysis System", Internal Los Alamos Report, LA-UR 86-748
- [4] J. A. Goldstone and A. C. Lawson, "Neutron Diffraction Study of Scandium Deuteride", LANSCE Experiment Reports, 1989 run Cycle, LA-11933-PR

Instrument used: (please type) Powder Diff. (NPD)	Local contact: G. Kwei, J. Goldstone	Proposal number: (for LANSCE use only) 900106
Title: Superconducting Superoxygenated Cuprates: Search for Phase Separation in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4+\delta}$		Report received: (for LANSCE use only) 7/11/91
Authors and affiliations: B. Morosin, G. H. Kwei**, J. E. Schirber*, J. A. Voigt*, E. L. Venturini*, and J. A. Goldstone**, *Sandia National Laboratories, Albuquerque, NM 87185 **Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>The metal oxides belonging to the K_2NiF_4 structure-type form an interesting class of materials with different subtle, but evidently important, structural modifications. Small changes in oxygen stoichiometry drastically alter the physical properties (from antiferromagnetic insulators to superconductors) as well as shift the phase boundary for structural phase transformations over large temperature ranges. The presence of excess interstitial oxygen has been shown to result in a complex behavior upon cooling which involves a phase separation in $\text{La}_2\text{CuO}_{4+\delta}$^{1,2} and $\text{La}_2\text{NiO}_{4+\delta}$³. One might also question if a similar phase separation occurs in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ because the differential broadening of the (400) and (040) Bragg peaks observed by Day et al⁴ at low temperatures is consistent with two phases having slightly different a-axes and essentially identical b-axes as found in $\text{La}_2\text{CuO}_{4+\delta}$.</p> <p>Normally as the Sr content increases, oxygen vacancies start to appear; however, high oxygen pressure annealing has been shown to allow the formation of samples without oxygen vacancies up to $x=0.36$.⁵ Since the interstitial oxygen is believed to be located at a site essentially tetrahedrally disposed with respect to either the neighboring oxide ions or La^{3+} ions, substitution with the larger ionic radii of Sr^{2+} might alter the excess oxygen interstitial concentration acceptable to the lattice.</p> <p>We have studied high pressure (2.3 kbar) high temperature (575°C) oxygen annealed ceramic $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4+\delta}$ by high-resolution neutron powder diffraction to determine its low temperature structural properties in comparison to similarly oxygenated $\text{La}_2\text{CuO}_{4+\delta}$. Unlike $\text{La}_2\text{CuO}_{4+\delta}$, the Sr-containing superconductor shows no low temperature phase separation. Further, the interstitial oxygen appears to be located at (1/4, 1/4, z) with</p>		

Experiment report (continued):

$z=0.163(5)$ and to have a value of δ consistent with $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4.019}$. Such a site is significantly displaced away from the interstitial location, $(1/4, 1/4, z)$ with $z \approx 0.25$ observed in $\text{La}_2\text{CuO}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$. The environment of such an interstitial site is suggestive of a smaller, neutral oxygen rather than a charged species.

(Paper submitted to Phys. Rev. B attached)

References:

1. J.D. Jorgensen, B. Dabrowski, S. Pei, D.G. Hinks, L. Soderholm, B. Morosin, J.E. Schirber, E.L. Venturini and D.S. Ginley, Phys. Rev. B38, 11337 (1988); references therein contain a detailed background review.
2. C. Chaillout, S-W. Cheong, Z. Fisk, M.S. Lehman, M. Marezio, B. Morosin and J.E. Schirber, Physica C158, 183 (1989); Physica C170, 87 (1990).
3. J.D. Jorgensen, B. Dabrowski, S. Pei, D.R. Richards and D.G. Hinks, Phys. Rev. B40, 2187 (1989).
4. P. Day, M. Rosseinsky, K. Prassides, W.I.F. David, O. Moze and A. Soper, J. Phys. C20, L429 (1987).
5. J.B. Torrance, A. Bezing, A.I. Nazzari, T.C. Huang, S.S.P. Parkin, D.T. Keane, S.J. La Placa, P.M. Horn and G.A. Held, Phys. Rev. B40, 8872 (1989).

Instrument used: <i>(please type)</i> NPD	Local contact: J.A. Goldstone	Proposal number: <i>(for LANSCE use only)</i> 192						
Title: Neutron Powder Diffraction Study of Calcium Ammonia Solvation Complexes in TiS_2		Report received: <i>(for LANSCE use only)</i> 3/14/91						
Authors and affiliations: <table border="0" style="width: 100%;"> <tr> <td style="width: 30%;">E.W. Ong</td> <td>Arizona State University</td> </tr> <tr> <td>J.A. Goldstone</td> <td>LANSCE</td> </tr> <tr> <td>W.S. Glaunsinger</td> <td>Arizona State University</td> </tr> </table>			E.W. Ong	Arizona State University	J.A. Goldstone	LANSCE	W.S. Glaunsinger	Arizona State University
E.W. Ong	Arizona State University							
J.A. Goldstone	LANSCE							
W.S. Glaunsinger	Arizona State University							
Experiment report: <p>The neutron powder diffraction patterns of two calcium-ammonia intercalates of titanium disulfide (host) were obtained. The stoichiometry of one compound is $(\text{NH}_3)_{0.04}[\text{Ca}^{2+}_{0.102}(\text{NH}_3)_{0.29}](\text{NH}_4^+)_{0.04}\text{TiS}_2^{-0.24}$. The other is $[\text{Ca}^{2+}_{0.132}(\text{NH}_3)_{0.26}]\text{TiS}_2^{-0.26}$. This study was stimulated by our finding that discrete calcium-ammonia complexes ($\text{Ca}(\text{NH}_3)_3$ or $\text{Ca}(\text{NH}_3)_2$) exist in the van der Waals (vdW) gaps of the host. Systematic x-ray diffraction studies suggest that these clusters are nearly planar.</p> <p>The present data indicates that the compounds do not adopt a 3-R structure as suggested by the x-ray studies. A number of Bragg peaks, not previously observed by x-ray, could not be indexed with $-h+k+l=3n$ or $h-k+l=3n$. The unit cell of the compounds is most likely a primitive type with trigonal symmetries.</p> <p>A surprising finding is that the neutron patterns fit better with a basal parameter of $\underline{a} = 6.84 \text{ \AA}$. This corresponds to a doubling of the basal parameter as derived from previous x-ray data ($\underline{a} = 3.42 \text{ \AA}$). This suggests that the contents within the vdW gaps, which are mostly weak x-ray scatterers, may be ordering to give a $2\underline{a} \times 2\underline{a}$ superlattice. Studies in the literature with Na^+ and Li^+ show cationic ordering near concentrations at $x=0.11$ and $x=0.25$. At the former concentration, a $\sqrt{3}\underline{a} \times \sqrt{3}\underline{a}$ superlattice is formed. The latter gives a $2\underline{a} \times 2\underline{a}$ ordering of the cations. The probable $2\underline{a} \times 2\underline{a}$ ordering of Ca^{2+} in our compounds ($x= 0.102$ and $x= 0.132$) may be a reflection of stronger electrostatic repulsions between the Ca^{2+} ions, as compared to those between Li^+ or Na^+.</p> <p>Further refinement of the data is in progress to determine the molecular geometry of the calcium-ammonia complexes.</p>

**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; 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 - 3 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 100° C
Sample size	0.5 - 10 mm ³
Experiment duration	1 - 5 days per octant of ??? space

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

Instrument used: <i>(Please type)</i> SCD	Local contact: Allen C. Larson	Proposal number: <i>(for LANSCE) use only</i> 3313
Title: Investigation of Texture of Course-Grained Metal Castings		Date received: <i>(for LANSCE only)</i> 2/13/91
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div>Anthony D. Rollett</div> <div>Center for Material Science Los Alamos National Laboratory Los Alamos, NM 87545</div> </div> <div style="display: flex; justify-content: space-between;"> <div>Phillip J. Vergamini</div> <div>P-DO LANL Los Alamos, NM 87545</div> </div> <div style="display: flex; justify-content: space-between;"> <div>U.F. Kocks</div> <div>Center for Material Science Los Alamos National Laboratory Los Alamos, NM 87545</div> </div> <div style="display: flex; justify-content: space-between;"> <div>Allen C. Larson</div> <div>LANSCE</div> </div>		
Experiment report: <p>Two depleted uranium samples, ca. 2 mm cubes, were cut from rods and examined. One rod was as cast material and the other swaged material. Both of these samples contained about 20% tungsten. The uranium in both samples is primarily α-phase. The 020, 002 and 111 uranium and the 110 tungsten poles from the two samples are given below. The pole figures in the first column are from the as cast material and the second column are from the swaged material. The contours in the as cast material pole figures for uranium are at intervals of 0.5 mrd (multiple of a random distribution) and all of the other pole figures are at 0.2 mrd. We see that for the as cast material, the uranium is very large grain with a limited number of crystal orientations and the tungsten is essentially in random orientation. The swaged rod material is essentially fine grain and shows strong preferred orientation.</p> <p>The analysis of these pole figures is in progress and will be reported later. At this point we can see that we can easily separate the pole figures for the two phases present in the samples. We have shown that high quality pole figures can be measured easily on high-Z materials using SCD.</p>		

Experiment report: (continued)

References:

Instrument used: <i>(please type)</i> SCD	Local contact: A. C. Larson	Proposal number: <i>(for LANSCE use only)</i> 3352.0
Title: Texture of High Temperature Superconductors		Report received: <i>(for LANSCE use only)</i> 2/22/91
Authors and affiliations: H. -R. Wenk University of California, Berkeley / Department of Geology & Geophysics A. C. Larson LANSCE- LANL K. Bennett University of California, Berkeley / Department of Geology & Geophysics A. Rollett CMS- LANL P. J. Vergimini LANSCE-LANL		
Experiment report: <p>The structure of the Bi-Sr-Ca-Cu-O ceramic superconductor (Bi-2212 where the numbers represent stoichiometric ratios of Bi:Sr:Ca:Cu) has been determined only recently¹. This permits indexing powder diffraction patterns reliably even though exact atomic positions of the Bi and Sr in these compounds are hard to quantify as positions seem to vary in displacements up to 0.4 Å². We present neutron texture analysis of a sample of the Bi-2212 rolled uniaxially using the SCD.</p> <p>Texture measurements of the same sample were collected with CuKα radiation at CMS at LANL. We compare the neutron data with the x-ray data. Figure 1 shows a comparison of d-spacing/two-theta spectra measured from both facilities and demonstrates the higher resolution capabilities of neutron scattering important for such closely spaced peaks.</p> <p>Figure 2 shows a) the (006), (008), and (0010) polefigures calculated at LANSCE and the histogram coverage and b) the (008) polefigure calculated at CMS. Calculations were deconvoluted using LANSCE polefigure programs and POPLA at CMS. We still hope to combine the two softwares. The correspondance of the (008) peaks even in the shape of the contours is excellent (LANSCE polefigures are inverted 180 degrees). In principle the three peaks from LANSCE should be identical but we suspect this to be due to the high intensity of the (008) peak relative to the (006) and (0010) which may be overlapped with other peaks or the background subtraction may be inadequate. There are similar discrepancies though not as large in the x-ray measurements; however, other x-ray techniques such as transmission were attempted at UCB this fall and failed.</p> <p>We feel neutron diffraction has the best potential thus far for texture determination of the bulk Bi-2212 compound³. We encourage texture determination of bulk superconductors in the future at LANSCE to characterize their anisotropy.</p>		

Experiment report (continued):

Figure 1

Figure 2

References:

1. Matheis, D.P., and Synder, R. L. (1990) The crystal structures and powder diffraction patterns of the bismuth and thallium ruddlesden-popper copper oxide superconductors. *Powder Diffraction* 5,1,8-25.
2. Gao, Y., Lee, P., Cappens, P., Subramanian, M.A., and Sleight, A. W. (1988) The incommensurate modulation of the 2212 Bi-Sr-Ca-Cu-O superconductor. *Science* 241, 954-956.
3. Rollet, A. T., Wenk, H. -R., Heidelbach, F. H., Schofield, T. G., Muenchausen, R.E., Raistrick, I. D., Arendt, P. N., Korzdera, D. A., Bennett, K., Kallend, J. S. (1990) Texture-property relationships in the high temperature superconductors. *Proc. 9th Int Conf. on Textures of Materials*, Avignon, France.

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
SCD	A.C. Larson	3353.0
Title:		Report received: <i>(for LANSCE use only)</i>
Preferred Orientation of Olivine		2/22/91
Authors and affiliations:		
H. -R. Wenk	University of California, Berkeley / Department of Geology & Geophysics	
A. C. Larson	LANSCE	
K. Bennett	University of California, Berkeley / Department of Geology & Geophysics	
G. Bussod	Bayerisches Geoinstitut	
Experiment report:		
<p>The intent of this project was to measure texture, preferred crystallographic orientation, of experimentally deformed peridotite using the SCD. Peridotite is a rock which constitutes 50-80% of the Earth's upper mantle. Understanding its rheology is imperative to understanding global convection and the tectonophysics of the Earth.</p> <p>The starting material was randomly oriented peridotite from Kilbourne Hole, New Mexico. The sample was deformed experimentally in a solid medium deformation apparatus by G. Bussod (Bayerisches Geoinstitut) to a partially molten state at $P_c=1013$ MPa, $T=1271$ K, $\dot{\epsilon}=2.07 \times 10^{-6} \text{ s}^{-1}$, $\sigma=246$ MPa, and $\epsilon=40\%$.</p> <p>Neutron diffraction was appropriate for this sample to resolve the closely spaced diffraction peaks of olivine and enstatite, the two main constituents of peridotite (Figure 1) and to measure the bulk sample. Despite this later advantage, we determined from our measurements at LANSCE that the measured portion of the sample was more coarse grained olivine with only a trace of enstatite and not representative of the whole sample. Nevertheless, this worked to our advantage. Simulated preferred orientations of peridotite by <i>Wenk et al.</i>, [1991]¹ have shown enstatite, the harder mineral (fewer slip systems), has little influence on the texture of olivine for aggregates up to 30% enstatite.</p> <p>We compare the polefigures for olivine obtained on the SCD to those of <i>Nicolas et al.</i>, [1973]² deformed experimentally at similar conditions but in a solid state. Discounting deformation by dislocation glide, olivine deforms in a slip regime by (010)[100], (001)[100], and (010)[001]. We expect the (010) poles to align with the direction of shortening and the (001) poles to rotate away. The polefigures from LANSCE resemble this behavior however the texture is not as strong as we would expect. Our (200) polefigure has four abnormally intense and randomly positioned peaks which we could not index to olivine or any other possible trace mineral in the sample. We suspect a deconvolution error which might account for the lower intensities in the other polefigures. The results suggest possible solid grain interaction in a partial melt can transmit stress.</p> <p>Figure 1: a) diffraction spectra for olivine and enstatite simulated for TOF neutron diffraction with GSAS. Peaks are indicated by tick marks directly above the horizontal abscissa. Upper row of marks refers to olivine, lower refers to enstatite b) indexed diffraction spectrum for olivine from LANSCE measurements</p> <p>Figure 2: (010), (001), (100) polefigures of a) experimentally deformed peridotites from <i>Nicolas et al.</i>, [1973] and b) experimentally deformed peridotite from Kilbourne Hole measured at LANSCE, sample GB1168</p>		

Experiment report (continued):

Figure 2

References:

- Wenk, H. -R., Bennett, K., Canova, G., Molinari, A. (1991) Modeling plastic deformation of peridotite with the self-consistent theory. *J. Geophys. Res.* in press.
- Nicolas, A. Boudier, F., and Boullier, A. -M. (1973) Mechanisms of flow in naturally and experimentally deformed peridotites. *Am. J. Sci.* 273, 853-876.

Instrument used: <i>(please type)</i> SCD	Local contact: A.C. Larson	Proposal number: <i>(for LANSCE use only)</i> 3354
Title: Development of Preferred Orientation in Experimentally Deformed Quartz Muscovite Aggregates		Report received: <i>(for LANSCE use only)</i> 2/22/91
Authors and affiliations: H.-R. Wenk, Dept. of Geology and Geophysics, University of California, Berkeley, CA 94720. J. Tullis, Dept. of Geological Sciences, Brown University, Providence, RI 02912 A.C. Larson, LANSCE, Los Alamos, NM 87545 P.J. Vergamini, LANSCE, Los Alamos, NM 87545 F. Heidelbach, Dept. of Geology and Geophysics, University of California, Berkeley, CA 94720		
Experiment report:		

Many rocks are composed of different minerals representing stronger and weaker components during deformation. In order to study the interaction between them and their influence on mechanical properties and texture development, we have chosen the model system quartz-muscovite. We performed axial compression experiments on pure quartz aggregates and those containing up to 50% muscovite. The three samples measured during the recent experiments were deformed under the following conditions:

<u>Specimen</u>	<u>Components</u>	<u>Temperature</u>	<u>Strain</u>	<u>Strainrate</u>	<u>Confining pressure</u>
W536	100% qtz	800°C	50%	10-6sec-1	1.5GPa
W537	50%qtz 50%ms	800°C	50%	10-6sec-1	1.5GPa
W538	50%qtz 50%ms	800°C	35%	10-6sec-1	1.5GPa

They complete a series of texture measurements with neutron diffraction at LANSCE which was started in 1989 (samples W502-506, see Fig.3).

Assuming an axisymmetric orientation pattern around the compression axis we only measured a section of the reciprocal space (Fig.1). The resulting raw data were processed with the software program GSAS at LANSCE and transformed into (partial) polefigures for different lattice spacings of quartz and muscovite (Fig.2). These were simplified by averaging the intensities along ϕ and the resulting profiles along χ show the intensity distribution for these planes from perpendicular ($\chi=90^\circ$) to parallel ($\chi=0^\circ$) to the compression direction (Fig.3). The distribution of the (001) poles of quartz could not be measured directly but was calculated from an ODF with the WIMV algorithm.

In all samples the quartz component has developed a c-axis maximum at 30° to 40° to the compression direction. With increasing amount of muscovite the strength of the quartz texture decreases drastically. The muscovite is preferentially oriented with its basal plane perpendicular to the compression axis. Both textures compare well with preferred orientations found in naturally deformed rocks.

Additional preliminary measurements of a granodiorite-mylonite containing quartz, biotite and feldspar were uncomplete because of the limited beamtime but revealed promising results. Even though the deconvolution of overlapping peaks in these samples remains to be a difficult problem we plan to extend the experiments in the near future.

Fig.1: Detector position (1-11) in projection of reciprocal space.

Fig.2: Partial polefigure of quartz (100), compression axis in the center

Fig.3: Profiles along χ for quartz (001), muscovite (004) and muscovite (110).

References:

S. Matthies & H.-R. Wenk (1985): ODF Reproduction with conditional Ghost Correction.- in: H.-R. Wenk (ed.): Preferred Orientation in Deformed Metals and Rocks: An Introduction to Modern Texture Analysis, 139-147, Academic Press, Orlando.

H.-R. Wenk, J. Tullis, F. Heidelbach, G. Canova & A.C. Larson (1990): Deformation and preferred orientation of quartz-muscovite mixtures: Experiments and Modeling.- EOS, Trans. Am. Geophys. Un., 71: 1657.

Instrument used: <i>(Please type)</i>	Local contact:	Proposal number: <i>(for LANSCE) use only</i>
SCD	Allen C. Larson	3355
Title: Dihydrogen Studies: $\text{IrH}_2\text{Cl}(\eta^2\text{-H})\text{P}(\text{i-Pr})_3)_2$		Date received: <i>(for LANSCE only)</i> 2 / 13 / 11
Authors and affiliations:		
Greg Kubas	INC-4 MS C346 Los Alamos National Laboratory Los Alamos, NM 87545	
Craig M. Jensen		
Allen c. Larson	INC-4 MS C346 Los Alamos National Laboratory Los Alamos, NM 87545	
Phillip J. Vergamini		
Experiment report:		
<p>The sample of $\text{IrH}_2\text{Cl}(\eta^2\text{-H}_2)\text{P}(\text{i-Pr})_3)_2$ which was provided for this diffraction experiment had not been deuterated and produced a very high background. We integrated 8500 reflection from 27 histograms using a d-spacing minimum of 0.75 Å. Of these only 4300 were measured at $I/\sigma_I > 1.0$ and about 2500 were stronger than $3 \sigma_I$. Refinements of the structure with these data produced no improvement over the x-ray results obtained previously. The final wR is ca. 0.10. Efforts to locate the $\eta^2\text{-H}_2$ entity were futile</p>		

Instrument used: <i>(Please type)</i> SCD	Local contact: Allen C. Larson	Proposal number: <i>(for LANSCE) use only</i> 3391
Title: Boron Carbide Structural Studies		Date received: <i>(for LANSCE only)</i>
Authors and affiliations: <div style="display: flex; justify-content: space-between;"> <div>Allen C. Larson</div> <div>LANSCE</div> </div> <div style="display: flex; justify-content: space-between;"> <div>Bruno Morosin</div> <div>Sandia National Laboratory Albuquerque, NM</div> </div>		
Experiment report: <p>Another attempt was made to collect data from a $^{10}\text{B}_4\text{C}$ crystal. Once again no diffraction maxima were observed. The</p> <p>A $^{11}\text{B}_4\text{C}$ specimen was found and 13 histograms were collected at 15K. This sample proved to consist of two crystalites. Sufficient data were collected from this pair of crystals to collect two unique data sets from the larger crystalite. The histograms were searched for diffraction maxima and then the maxima were indexed to match two crystalites. The locations of these maxima were used to refine the lattice constants to give $a=5.5992(3)$ and $c=12.0624(9)\text{\AA}$, the room temperature lattice constants measured with x-rays are $a=5.6039(4)$ and $c=12.0786(14)\text{\AA}$.</p> <p>The diffraction data from the two crystalites were integrated and a least-squares refinement of the structure including anisotropic thermal parameters on all atoms was carried out.</p>		

Instrument used: <i>(please type)</i> SCD	Local contact: Dr. Allen Larson	Proposal number: <i>(for LANSCE use only)</i> 3358
Title: STRUCTURE OF THE BICYCLO[1.1.1]PENTANE RING SYSTEM		Report received: <i>(for LANSCE use only)</i> 3/8/91
Authors and affiliations: Josef Michl and Piotr Kaszynski Center for Structure and Reactivity Department of Chemistry and Biochemistry University of Texas at Austin Austin, TX 78712-1167 After June 1, 1991: Department of Chemistry and Biochemistry University of Colorado Boulder, CO 80309-0215 Allen Larson, LANSCE		
Experiment report: We are interested in the bicyclo[1.1.1]pentane structure 1: <div style="text-align: center;"> </div> <div style="text-align: center;">1</div> <p>We are engaged in an attempt to develop a molecular-size "Tinkertoy" construction set for the assembly of artificial solids with pre-designed properties. The straight rods in this molecular civil engineering system are oligomers containing several bicyclo[1.1.1]pentane cages. They are to be attached to connectors through functional groups located at both ends of the rods.</p> <p>A detailed structural and spectroscopic characterization of the basic elements of the proposed construction set is needed. While we were able to obtain reliable data on the location of the heavy atoms in about ten of these staffs by X-ray diffraction, none provided information on the location of the hydrogens. The problem of the exact location of hydrogen atoms in the CH₂ groups of bicyclo[1.1.1]pentane attracted attention soon after this hydrocarbon was first made. The hydrocarbon is unusual because of the very short non-bonded C - C distance (1.845 Å), high degree of cyclobutane ring puckering (120°), small C-CH₂-C angle (73.3°), and high strain energy (68 kcal/mol).</p>		

Experiment report *(continued)*:

Last year, we attempted to identify the hydrogen positions by single-crystal neutron diffraction, using a crystal of a deuterated diketone ($1, X = CD_3CO$) but found the structure to be too disordered to permit a solution.

References:

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
SCD	P. Vergamini	900601
Title: Study of preferred orientation in silver-clad superconductor: $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$		Report received: (for LANSCE use only)
2/13/91		
<p>Authors and affiliations:</p> <p>Eric Hellstrom, Department of Materials Science and Engineering, University of Wisconsin-Madison, 1509 University Ave., Madison, WI 53706</p> <p>Phillip Vergamini, Los Alamos National Laboratory, LANSCE</p> <p>Allen Larson, Los Alamos National Laboratory, LANSCE</p>		
<p>Experiment report:</p> <p>This experiment showed (1) that a stack of Ag-clad BSCCO "2212" ($\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$) flat wires could be assembled and analyzed by neutron diffraction, (2) that the "2212" in the melt-processed wire was textured with the C-axis perpendicular to the plane of the wire, (3) that there was no texture in the a-b planes, and (4) that the Ag-cladding showed the standard recrystallization texture.</p> <p>A stack of 30 layers of Ag-clad BSCCO superconducting wire each $100\mu\text{m}$ thick with an overall cation mole ratio of 2:2:1:2 Bi:Sr:Ca:Cu was assembled. The wire had undergone melt processing, where it had been heated to 920°C, cooled to 840°C, then annealed at 840°C [1-3]. The cooling and long-term anneal caused the "2212" to align within the wire.</p> <p>The mechanism that causes "2212" to align within the Ag-cladding is unknown. One suggestion for alignment is an epitaxial relation between the Ag and "2212".</p> <p>This experiment was designed to determine if there were (1) an epitaxial relation between the "2212" and the Ag-cladding and (2) texture within the a-b planes. Figure 1 is a (111) pole figure for Ag showing the classic Ag recrystallization texture. Figure 2 is the "2212" (008) pole figure, which shows C-axis alignment normal to the plane of the wire. Although the pole figures in Figs. 1 and 2 suggest there may be epitaxy between the Ag and 2212, we cannot determine if an epitaxial relation between the "2212" and Ag causes alignment of the "2212".</p> <p>Figure 3 shows the (220) pole figure for "2212". There does not appear to be any preferred texture within the "2212" a-b planes as seen by the relatively uniform intensity in the equatorial region. However, this figure also shows (220) intensity in the central region, indicating that the "2212" C-axis alignment is less than perfect. This imperfect texture shown by the (220) pole figure for the neutron diffraction experiments agrees with Rollett's (of LANL) recent x-ray pole figures of melt processed "2212", and optical microscopy we have done at UW-Madison on the melt-processed wire that shows a range of C-axis orientations within the wire [5]. The (008) and (220) pole figures (cf. Figs. 2 and 3) suggest that "2212" is predominantly aligned with the C-axis perpendicular to the plane of the flat wire with some grains oriented with their C-axis parallel to the plane of the wire.</p>		

Experiment report (continued):

Fig. 1. Ag (111) pole figure.

Fig. 2. "2212" (BSCCO) (008) pole figure.

Fig. 3. "2212" (BSCCO) (220) pole figure.

References:

1. R.D. Ray and E.E. Hellstrom, J. Appl. Phys. 57 (1990) 2948
2. R.D. Ray and E.E. Hellstrom, Physica C 172 (1991) 435
3. R.D. Ray and E.E. Hellstrom, "Ag-clad Bi-Sr-Ca-Cu-O wires: II. Important factors in supersolidus phase studies, accepted for publication in Physica C.
4. A. Rollett, DARPA/DOE workshop on high-temperature superconductors, Santa Fe, NM Jan. 31, Feb. 1, 1991.
5. R.D. Ray and E.E. Hellstrom, Reported at the Fall meeting of the Materials Research Society, Boston, MA, 1990.

Instrument used: <i>(Please type)</i>	Local contact:	Proposal number: <i>(for LANSCE) use only</i>
SCD	Allen C. Larson	900604
Title:		Date received: <i>(for LANSCE only)</i>
Neutron Diffraction Study of a Chiral Oxazinone		

Authors and affiliations:

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Allen C. Larson LANSCE

Experiment report:

A series of chiral oxazinones have been prepared. A typical example is shown in Fig. 1. These compounds tend to add hydrogen across the double bond between C2 and C3 with 95% stereo specificity. The crystal structure as determined by x-ray diffraction did not provide accurate positions for the hydrogen atom on C3. Therefore a set of neutron diffraction data were collected to see if the hydrogen on C3 was displaced in a manner which would predispose hydrogen to add preferentially on one side rather than the other.

Figure 1.

The compound with R1 as a methyl group and R2 as an isopropyl group, partially deuterated, was used for the neutron diffraction experiment. The isopropyl group, C5 and C6 were deuterated and C1, C3 and the methyl group were not. This resulted in the chemical formula, $C_{10}H_5D_{10}O_3N$.

The crystal is orthorhombic, space group $P2_12_12_1$, $a = 6.8188(7)$, $b = 7.4060(8)$, and $c = 20.1140(22)$. Ten histograms of data were collected at 15K. The unit cell parameters were refined using 961 reflection positions whose maxima were greater than 100 counts per pixel. The reflection data in these histograms was integrated to yield about 250 reflections per histogram, for a total of 2546 reflections observed at greater than $1.5 \sigma_I$.

Experiment report: (continued)

All of the hydrogen and deuterium atoms were located from a delta-F Fourier map computed with phases defined by the heavy atoms. These were added to the structural model and the position and thermal motion parameters for all atoms as anisotropic were refined. This refinement yielded a final $R = 0.057$ and $R_w = 0.045$. The C-H distances range from 1.073(7) Å to 1.110(4) Å with an average value of 1.092 Å. The oxygen atoms in the rings have O-C bonds of 1.375(3) and 1.440(4) for O1 and 1.366(3) and 1.446(3) for O2. The N-C distances are N-C1, 1.437(3) Å, N-C4, 1.369(3) Å, and N-C5, 1.477(3) Å.

Unfortunately the hydrogen on C3 lies very nearly in the plane defined by R1, C2 and C3. Thus explanation for the high stereo specificity of hydorgenation of the C2-C3 double bond still is lacking. The results of this refinement will be used in defining a mechanistic model which will be tested for its ability to explain the above problem.

References:

None

Instrument used: <i>(Please type)</i>	Local contact:	Proposal number: <i>(for LANSCE) use only</i>						
SCD	Allen C. Larson	900605						
Title: Preferred Orientation in Fossil Coral		Date received: <i>(for LANSCE only)</i>						
Authors and affiliations: <table> <tr> <td>J. Post</td> <td>Smithsonian</td> </tr> <tr> <td>R.B. Von Dreele</td> <td>LANSCE</td> </tr> <tr> <td>Allen C. Larson</td> <td>LANSCE</td> </tr> </table>			J. Post	Smithsonian	R.B. Von Dreele	LANSCE	Allen C. Larson	LANSCE
J. Post	Smithsonian							
R.B. Von Dreele	LANSCE							
Allen C. Larson	LANSCE							
Experiment report: <p>Chalcedony is one of a group of natural quartz minerals which grow with a fibrous texture. In chalcedony the fibers are parallel to the direction of crystal growth. Since quartz crystalizes in space group $P3_121$ one would normally expect that these fibers would have (001) as their principle axis. However optical measurements on various chalcedony samples seem to indicate that the fibers grow along (110). Also massive quartz crystals tend to be elongated along (110).</p> <p>A fragment of chalcedony, ca. 2 mm by 2. mm by 2.5 mm was mounted with the sample growth direction nearly parallel to the Phi axis of the SCD instrument. We measured 27 histograms to obtain complete pole figures for the (100), (011), (110), (111), (112), (012), (200), and (021) planes. These poles are shown on the next page and clearly show that the fibers are oriented with (110) parallel to the growth direction.</p> <p>The plots are contoured at intervals of 0.1 mrd (multiples of a random distribution).</p>								

Experiment report: (continued)

$Q=100$
 $\sigma = 4.18$

$Q=110$
 $\sigma = 2.46$

$Q=112$
 $\sigma = 1.62$

$Q=111$
 $\sigma = 2.24$

$Q=011$
 $\sigma = 2.34$

$Q=012$
 $\sigma = 2.28$

$Q=021$
 $\sigma = 1.68$

$Q=000$
 $\sigma = 2.12$

References:

R.B. Sosman (1965) *The Phases of Silica*, Rutgers Univ. Press, New Brunswick, NJ

Instrument used: <i>(Please type)</i>	Local contact:	Proposal number: <i>(for LANSCE) use only</i>
SCD	Allen C. Larson	900603
Title: Garnet for SCD Documentation		Date received: <i>(for LANSCE only)</i>
Authors and affiliations: Allen C. Larson LANSCE		
Experiment report: <p>A small, ca. 1.5 mm³, natural garnet was examined with the intent of collecting data which would be made available to SCD users for processing to become familiar with SCD and the analysis of it's data. Garnet being cubic, point group <i>m3m</i>, requires only five or six histograms for a complete data set. This has several advantages for an example to be provided to a user. First, it is a very small data set, and will process quite rapidly. Secondly it will illustrate the steps needed to optimize the data collection. Thirdly, the structure being highly symmetric, has few parameters and all refinements will go very quickly.</p> <p>Unfortunately the sample proved to be two crystals missoriented by about 1.5°. The data hence will not be suitable for it's original intent, but will be used for the development and testing of procedures for handling such samples.</p>

**Low-Q Diffractometer
(LQD)**

Low-Q Diffractometer (LQD)

The Low-Q Diffractometer (LQD) is designed for studying structures with dimensions in the range 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 – 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 a 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

Instrument Used: LQD	Local Contact: Phil Seeger	Proposal #: 3306
Title: Microstructure of Inverse Micelles Near the Upper Critical Consolute Point.		Report Rec'd
Authors and Affiliations: Jess Wilcoxon, Organization 1153, Sandia National Labs, Albuquerque, N.M.		5/31/91

Experimental Report:

The purpose of this experiment was to learn more about the microstructure and interactions of nonionic inverse micelle systems. The surfactant systems investigated had the generic formula $\text{CH}_3(\text{CH}_2)_i(\text{OCH}_2\text{CH}_3)_j\text{OH}$, which we abbreviate as C_iE_j in the following report. 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. In our experiments we exploited this ability by combining some rather hydrophilic surfactants (e.g. C_6E_5 , C_7E_5 , and C_{10}E_8) with hydrophobic solvents (e.g. dodecane (C_{12}) - hexadecane (C_{16})). This resulted in the presence of a two phase boundary with an upper critical consolute point in an experimentally accessible region. We approached the phase boundary by variation of the temperature observing the scattering behavior in both the single and two phase regions. We provided a highly stable external circulating bath for temperature regulation.

Our previous work[1,2] using static and dynamic light scattering in the $\text{C}_{10}\text{E}_8/\text{C}_{12}$ system indicated that critical fluctuations would play a very important role in the interpretation of scattering in the long wavelength (i.e. light scattering) limit and probably obscure information concerning microstructure. Thus, for example, dynamic light scattering could not be used to obtain micelle radii due to the effects of critical slowing down. Figure 1 shows our SANS results combined with previous light scattering data.

Figure 1. Combined SANS and light scattering data for an inverse micelle system.

The data shows a dramatic increase in $I(Q=0)$ with reduced temperature ($\epsilon=(T-T_c)/T_c$, T_c =critical temperature). The momentum transfer, Q over the range $Q=0.0002 \text{ \AA}^{-1}$ to $.07 \text{ \AA}^{-1}$ depends only on the correlation length ξ , which increases dramatically from $66 \text{ \AA}$ to $607 \text{ \AA}$ as indicated. It is clear from this figure that SANS information concerning microstructure is strongly affected by the attractive intermicellar interactions in this system. It is also clear that attempting to obtain information on the static correlation length of these solutions from SANS alone is not feasible because of SANS resolution limitations.

To separate the effect of interactions and microstructure we studied the effect of surfactant concentration on the scattering behavior. Partial results are shown in figure 2. The data were obtained at approximately equal distances ($\sim 7^\circ\text{C}$) from the two phase boundary and it is observed that the value of R_g , obtained from standard Guinier analysis, is largest near the critical concentration. The limiting slope of -4 is consistent with droplet-like micelle geometry but the value of $R_g \sim 56 \text{ \AA}$ is larger than would be anticipated from the known surfactant chain length, reflecting the effect of interactions. Similar measurements on the C_6E_5/C_{12} system, reveal a limiting slope of -2, consistent with two-dimensional, disc-like micelles. The value of R_g , obtained from SANS scattering data at large distances from the critical points in both concentration and temperature was $23 \text{ \AA}$. This smaller value reflected the fact that this surfactant has a significantly shorter chain length, but still is larger than would be expected from the surfactant chain length. In this system there is also a significant dependence of R_g on wt% surfactant, this value peaking on the critical isochore. Thus, both SANS and light scattering measurements must account for the effect of interactions in any analysis of scattering data. However, these values are probably quite close (10-20%) to the "bare" micelle size.

Figure 2. Intensity per surfactant concentration (I/c) from combined light and SANS data at a large temperature distance ϵ from the two phase boundary.

Even larger dependences of the scattering on concentration are observed quite close to the two phase boundary. Figure 3 shows such combined light and SANS measurements

obtained on the C₁₀E₈/C₁₂ system. There is roughly an order of magnitude increase in the apparent mass (I/c), on moving toward the critical isochore.

Figure 3. Intensity per surfactant concentration (I/c) from combined light and SANS measurements as a function of wt% surfactant near the two phase boundary, at a temperature distance ϵ . Dramatic increases in the apparent mass, I/c , are observed upon moving toward the critical isochore.

Finally, we examined the structure in the coexisting upper and lower phases. The neutron beam for this sample was ascertained to be solely in one phase by visual observation. SANS data alone revealed no significant qualitative differences from that shown above for the single phase region, nor between the two phases. However, when this data was combined with light scattering measurements, at roughly the same distance ϵ from the two phase boundary, the behavior shown in figure 4 was obtained. The behavior at large Q (small length scales) is consistent with small, weakly interacting, disc-like micelles. For example, the correlation length, ξ , obtained solely from SANS data is significantly smaller than observed in the single phase region at an equivalent distance, ϵ . However, smooth interfaces are present on large length scales as evidenced by the Porod behavior seen with light scattering. These large structures are typically observable for periods exceeding many days, and are apparent remnants of the phase separation process, perhaps caused by the vertical migration of surfactant from one phase to the other. This behavior is observed in water-continuous micelles as well.[3]

Figure 4. Intensity I vs momentum transfer Q shows smooth interfaces are formed (Porod's law behavior) at large length scales (>100 nm) during the phase separation process.

References:

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- [2] Wilcoxon J.P., Critical Behavior of Inverse Micelles Systems, in Dynamics in Small Confining Systems, Symposium M, *Proceedings of the Fall Meeting of the Materials Research Society*, Boston, MA, (1990).
- [3]. Wilcoxon J.P., Phase Behavior and Metastability in a Non-Ionic Surfactant-Water-Electrolyte System, *J. Phys. Chem.*, 94, 7588, (1990).

Instrument used: <i>(please type)</i> LQD	Local contact: Phil Seeger	Proposal number: <i>(for LANSCE use only)</i> 3310.0
Title: Micelle-Vesicle Equilibria and Transitions in Surfactant Solutions		Report received: <i>(for LANSCE use only)</i> 2/25/91
Authors and affiliations Eric W. Kaler Department of Chemical Engineering University of Delaware Newark, Delaware 19716 Jess Wilcoxon Sandia National Laboratory Div. 1153 Albuquerque, New Mexico 87105		
Experiment report: <p>We were awarded one day of beam time to carry out measurements on samples representative of a family of newly-discovered spontaneous vesicles. In addition, we attempted to measure some transition structures between micellar and vesicular phases in mixtures of bile-salt and lecithin, but were unable to do so because of time limitations.</p> <p>A series of vesicle solutions were made up at 1% total surfactant concentration in D₂O and with various ratios of anionic surfactant (sodium dodecylbenzene sulfonate - SDBS) and cationic surfactant (cetyl trimethyl ammonium tosylate - CTAT). Vesicles exist, and form spontaneously, in these phases as documented by electron microscopy and light scattering (Kaler et al. <i>Science</i> <u>245</u>, 1371 (1989)). A representative sample of the scattering spectra (Figure 1) from the SBDS-rich portion of the phase diagram shows the characteristic decay of $I(q)$ with q^2 in the low-q region and a cross-over to q^{-4} decay at high q. From the q^2 region a thickness of the bilayer membrane can be estimated to be ca. 40Å. The cross-over to Porod's Law is at q ca. 0.03, so that $q_{\text{crossover}}^{-1} = 33 \text{ Å}$, a result consistent with scattering from a membrane.</p> <p>Detailed modelling of these scattering curves is underway. We note that these vesicles are about 500 Å in diameter, so that the form factor scattering would show a series of maxima and minima in the observable q-range. Although size polydispersity will damp these oscillations, they should still be observable in the spectra. That they aren't suggests that we have passed the limit of resolution of LQD. In preliminary results, desmearing of the spectra of similar samples measured at ORNL does show oscillations. Finally, more concentrated dispersions of these vesicles are in an interesting region of colloid stability. Because the vesicles are large and the ionic screening is weak, the product of the inverse Debye length K and the diameter a is about 10. This exceeds the limit of applicability of the usual DLVO potential used, with the Mean-Spherical Approximation, to calculate $S(q)$ for charged colloidal particles. Thus we are developing an alternate calculation for $S(q)$ in this limit.</p>		

Experiment report (continued):

Figure 1: Log-log plots of scattering curves from several vesicle dispersions formed at different anionic:cationic surfactant ratios. The low q line has a slope of -2, and the high q line a slope of -4.

References:

Instrument used: <i>(please type)</i> LQD	Local contact: R. P. Hjelm P. A. Seeger	Proposal number: <i>(for LANSCE use only)</i> 3325-0
Title: Surface Interaction Between Active Carbon Black Surfaces and Elastomeric Chains		Report received: <i>(for LANSCE use only)</i> 2/14/91
Authors and affiliations: Wesley A. Wampler, Sid Richardson Carbon Co., Fort Worth, TX Michel Gerspacher, Sid Richardson Carbon Co., Fort Worth, TX J. B. Donnet, Universite de Haute-Alsace, Mulhouse, France		
Experiment report: <p>Background: Carbon black is a filler essential to the rubber industry. Its most remarkable quality is its ability to significantly increase the strength of rubber, and it is thus given the term reinforcing filler¹. The improved mechanical properties imparted by carbon black to a polymeric system is essential to the overall performance of the end use product --- automobile and truck tires are prime examples. The mechanism of this reinforcement at low strain has been attributed to carbon black networking²; however, several aspects of the general mechanism of reinforcement are still unclear. Obviously any further elucidation of factors which clarify the carbon black reinforcement mechanism of elastomers is a great practical and academic importance.</p> <p>Small-angle neutron scattering (SANS) is being used to determine the conformation of the elastomer and the spatial distribution of the elastomer and carbon black in various compounded mixtures of the two. The compounds are first extracted with a suitable solvent to remove the soluble elastomer segments. The resulting carbon black/"bound" rubber gel is then dried and the content of "bound" rubber is determined. The carbon black/"bound" rubber phase is then swelled in a selected solvent to reconstitute the gel. For interpretation of the results, the swollen elastomer-carbon black system is treated as a simple, two component system. To accomplish this the scattering length density of the solvent, ρ_s is varied by mixing deuterated and protonated solvent such that a contrast variation study is done. Cyclohexane is particularly good in this regard, for studies of the carbon black-elastomer mixtures under investigation, since ρ_s is varied between $-0.28 \times 10^{10} \text{ cm}^{-2}$ for 100% C_6H_{12} to $6.68 \times 10^{10} \text{ cm}^{-2}$ for C_6D_{12}. Thus it is possible to contrast match the carbon black ($\bar{\rho}_{\text{CB}} = 6.2 - 6.4 \times 10^{10} \text{ cm}^{-2}$ or the elastomer ($\bar{\rho}_E = 1 \times 10^{10} \text{ cm}^{-2}$), and thus assess the distribution and conformation of the other component</p>		

Experiment report (continued):

in the mixture. Of interest is the degree of agglomeration of the carbon black, the form of the "bound" elastomer layer, and a determination of the chain statistics of "bound" elastomer with respect to the bulk material.

Results: During the past run cycle some preliminary measurements were made on different carbon blacks and two elastomers, polyisoprene and styrene butadiene rubber (SBR). Each component was examined by itself, and carbon black/elastomer compounds were also examined. The contrast match point of the carbon black was determined in a contrast variation study using SANS and found to be very similar to the contrast match point calculated through chemical composition and density. Assessment of the data is not complete and additional data will be necessary for the final analysis, but preliminary analysis reveals some new information about the rubber distribution and conformation not available in earlier studies. Measurements on the rubbers by themselves swelled in the solvent indicated the presence of extended Gaussian chains. In the solvent-swelled gels of carbon black and elastomer, the chain conformation appeared more extended than the virgin rubber. Further, in these mixtures the elastomer appeared to be localized in globules measuring roughly 200 Å across. This is in contrast to carbon black which by itself appears to form an extended, random ("fractal") network.

Figure 1: SANS results for Polyisoprene/Carbon Black
in $\text{C}_6\text{D}_{12}/\text{C}_6\text{H}_{12}$ (95/5)

References:

- 1 Donnet, J.B., and Voet, A., "Carbon Black, Physics, Chemistry and Elastomer Reinforcement", Marcel Dekker, Inc., New York (1976)
- 2 Gerspacher, M., et al, "Carbon Black Networking", invited lecture at International Rubber Conference in Paris, June 1990

Instrument used: (please type) LQD	Local contact: R. HJELM	Proposal number: (for LANSCE use only) 3331
Title: SANS of the ATP'ase Coupling Factor CF1		Report received: (for LANSCE use only) 3/4/91
Authors and affiliations: Rex P. Hjelm LANSCE, Los Alamos National Laboratory, Los Alamos, NM P. Thiagarajan IPNS, Argonne National Laboratory, Argonne IL E.M. Moudrianakis, Department of Biology, The Johns Hopkins University, Baltimore, MD		
<p>INTRODUCTION: The ATP Synthetase from energy transducing membranes of chloroplasts, mitochondria and bacteria couples the electrochemical energy generated by electron transport with the synthesis of ATP. This coupling factor is composed of two parts. One is an extrinsic membrane protein which synthesizes ATP and is called F1, CF1 or BF1 for mitochondrial, chloroplast, or bacterial factor 1, respectively. The other is an intrinsic membrane protein (called Fo, CFo or BFo) which conducts protons through the membrane. The extrinsic portion is easily purified and has a molecular weight of 360 KDa to 400 KDa, depending on the source. It is the soluble extrinsic fraction that we will be studying. The extrinsic protein is known to contain 9 subunits of five different types: three each of alpha and beta and one each of gamma, delta and epsilon [1]. The general geometry is thought to be a hexamer ring of alternating alpha and beta subunits asymmetrically arranged within the ring and a stalk which connects this complex with the membrane bound portions [1,2]. Electron microscopy of "negatively stained" ATP Synthetase gives a low resolution picture of the complex as a spherical 90-100A diameter particle with a dark staining center (hydrophilic cavity) or hole [3]. The enzyme complex can be readily dissociated and reconstituted [1,5]. It can be isolated from organisms which can be deuterated; thus by way of reconstitution a specific component can be labelled. Large rearrangements are observed in vitro with the isolated and purified ATP Synthetase and have been monitored as alterations in enzymatic properties, in binding of effector molecules [6,7], and in electrophoretic mobilities [8]. These transformations can be reproducibly controlled by specific physiologically relevant treatments. Thus the different putative states can be readily produced for structural studies.</p> <p>RESULTS: Measurements were made on the CF1 complex from spinach chloroplasts in 100%, 80% and 0% D₂O. Protein concentration was 7 g/l. The number of measurements was limited by the failure of the liquid hydrogen moderator. The data were placed on an absolute scale, and are shown in Figure 1. Guinier analysis was used to estimate the radii of gyration from each contrast as 57Å in 100% D₂O, 56Å in 80% D₂O, and 42Å in H₂O. The values in 100 and 80% D₂O agree with previous SAXS determinations [4]. The large difference between these and that found in water suggests nonuniform distribution of scattering length density in the particles. Extrapolation to $Q \rightarrow 0$ gives an estimate of $S(Q)$. These are shown in Figure 2 as $\sqrt{S(Q)}$ verses the solvent scattering length density, ρ. The slope of the gives an estimate of the molecule volume as $290 \pm 20 \text{ nm}^3$. The average particle scattering length density is estimated at $1.7 (0.5) \times 10^{10} \text{ cm}^{-2}$.</p>

REFERENCES:

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2. Amzel, L.M., and Pederson, P.L. (1983), *Ann. Rev. Biochem.*, **52**, 801-823.
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Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
Low-Q Diffractometer	P. Seeger	3336.0
Title: Droplet-to-Lamellar Transition in AOT/water/n-decane Microemulsion System		Report received: <i>(for LANSCE use only)</i> 12/17/90
Authors and affiliations: M. Kotlarchyk and S. M. Ritzau (Rochester Institute of Technology, Dept. of Physics, Rochester, NY 14623)		
Experiment report: <p>Small-angle neutron scattering experiments were performed at the Los Alamos Neutron Scattering Center to investigate the high temperature L_α phase in the AOT/water/decane microemulsion system.¹ The system was modelled as randomly oriented lamellar stacks with a one-dimensional paracrystalline distortion.² For samples injected into cells at high temperature (49°C), the two-dimensional Q-maps show anisotropic scattering consistent with partial alignment of the L_α phase, while samples injected near room temperature (25°C) exhibit isotropic scattering produced by a previously observed³ isotropic dense droplet L_2 phase. From the L_α spectra, it was found that a stack typically contains about 15 lamellae, about 80 Å apart. Each layer is coated by a diffuse surfactant interface with a characteristic thickness of approximately 9 Å. The fact that the scattering spectra do not exhibit maxima beyond the first order is explained by the observation that the Hosemann g-factor⁴ gives about a 20% variation in the interlamellar spacing. The mean spacing is inversely proportional to the surfactant concentration as expected for a lamellar phase. Overestimation of the zero-order scattering predicted by the employed paracrystal model is attributed primarily to improper treatment of the contrast between each layer and the space-filling lamellar matrix.</p>

Figure 1. Small-angle neutron scattering spectra from unaligned high-temperature L_α phase for three volume fractions and best-fit curves from paracrystal model. The bottom data set is from a room temperature droplet phase microemulsion shown for comparison. The paracrystal model does not successfully fit this latter spectrum.

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Instrument used: (please type) Low q Diffractometer	Local contact: R. Hjelm P. Seeger	Proposal number: (for LANSCE use only) 5338
Title: Polymer/Surfactant Interactions: A Structural Study		Report received: (for LANSCE use only) 3/12/91
Authors and affiliations: Greg Beaucage, R. S. Stein, D. A. Tirrell Department of Polymer Science and Engineering University of Massachusetts Amherst, MA H. Schild Central Research Polaroid Corporation Cambridge, MA		
Experiment report: The structural interaction between polymers and surfactants has been used industrially to drastically alter the viscosity of dilute polymer solutions, to enhance the adsorption of oil by surfactants and to enhance the aqueous solubility of synthetic polymers. Additionally, these systems are of great interest in the production of 'biological-like' complex microstructures. The classic system in this field of research is Polyethyleneoxide (PEO)/SDS. A general observation is that as the concentration of SDS is increased in dilute aqueous solutions of PEO two critical concentrations are observed, T_1 and T_2 ¹ . Generally, T_1 corresponds to the SDS concentration at which polymer bound micelles begin to form and is independent of PEO concentration. T_2 corresponds to the concentration of SDS at which saturation of the polymer chains with bound aggregates occurs and is linearly proportional to the PEO concentration. Cabane and Duplessix ² have applied neutron scattering using the method of contrast variation to this system. In this work it was determined that spherical clusters of SDS form along PEO chains, T_1 corresponding to the concentration at which these clusters first form with increasing numbers of these clusters forming with increasing concentration of SDS until T_2 is reached at which point saturation of the PEO chains occurs. This model has been used extensively to explain drastic changes in physical properties of these solutions which occur at T_1 and T_2 . This CAC behavior has been successfully predicted by theoretical models of Nagarajan ³ and Ruckenstein ⁴ which assume the described structure for the complex.		

Experiment report (continued):

In the experiment done at LANSCE (10/90), the generality of the Cabane/Duplessix structure was to some extent demonstrated using poly(N-isopropylacrylamide) (PNIPAAM) (synthesized at UMASS^{5,6}) and the surfactant sodium n-dodecyl sulfate (SDS). Using a combination of Guinier, Kratky, and Porod plots as well as Fourier transforms of the scattering patterns it was determined that this system probably forms a modified grapevine structure at room temperature and in a specific concentration regime. A dilute aqueous solution of PNIPAAM forms random coils with diffuse boundaries of about 165Å diameter. A dilute solution of SDS forms micelles of about 40Å diameter with sharp boundaries. A dilute mixture of the two at room temperature form a swollen structure with diameter of about 325Å, diffuse boundaries and containing rod like SDS with domains of average diameter 40Å and sharp boundaries. This is believed to be a swollen coil with a chain coated by SDS protecting it from interaction with water. Measurements were made on the bulk structure at two temperatures above room temperature. PNIPAAM displays an LCST (phase separation with an increase in temperature) in aqueous solution of about 34°C. The structure of the complex at 40°C, as measured by SANS, transforms from a swollen coil to a rod of average diameter 200Å and sharp boundaries (SDS coat). On further raising the temperature to 60°C a swollen coil of about 300Å diameter is obtained with very sharp boundaries indicating the SDS may coat the outside of the swollen coil. These rich structural transitions are only the beginning of the possibilities in this system. Recently⁷, work has been done in Switzerland using quasi-elastic light scattering on the same system which indicates dramatic structural transitions as a function of concentration of SDS at temperatures above the LCST of PNIPAAM. A distinction between *inter- and intra-molecular miscibility* has been proposed, that is miscibility in which aggregates of the immiscible species are prevented from forming (supramolecular) and miscibility in which submolecular miscibility occurs. The extension of these concepts, and the equations which describe them, to polymer/polymer blend systems may be of great technical value.

References:

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- ⁵Schild, H. G.; Tirrell, D. A. *Polymer Preprints* **1989**, **30**(2), 350.
- ⁶PhD Thesis, Schild, H. G., Department of Polymer Science, University of Massachusetts, Amherst, December **1989**
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Instrument used: <i>(please type)</i> Low Q Detector	Local contact: Rex Hjelm	Proposal number: <i>(for LANSCE use only)</i> 3340.0
Title: "Small Angle Neutron Scattering of Block Copolymers in Solution"		Report received: <i>(for LANSCE use only)</i> 3/26/91
Authors and affiliations: Alice P. Gast, Kathy A. Cogan and Jenni Raeder Department of Chemical Engineering Stanford University Stanford, CA 94305-5025		
Experiment report: <p>We have undertaken a study of polymeric micelle structure in dilute solution. In previous work employing dynamic light scattering (1), static light scattering (2) and small angle x-ray scattering (3), we have shown that the concept of a star-like micelle having a dense core of insoluble chains surrounded by a corona of semi-dilute arms holds quite well. It was our intention with neutron scattering to probe the details of the structure in the micellar corona. To do this, we purchased polystyrene-block-d-methylmethacrylate (PS-dPMMA) from Polymer laboratories. This polymer when suspended in deuterio-cyclohexane will have a core nearly contrast matched leaving the scattering from the micellar corona evident.</p> <p>To form micelles from PS-PMMA diblock copolymers they must be heated beyond the glass transition temperature of the constituent polymers, above 100 C. We formed dilute stock solutions of PS-dPMMA, $M_w=121,300$, 50% PS, in d-cyclohexane by heating over night in closed vessels. Upon cooling to 40 C, the micelles were very monodisperse, having hydrodynamic radii of 40 nm. Solutions were then concentrated to 0.3 wt% and suspended in mixtures of d-cyclohexane and h-cyclohexane. We performed small angle neutron scattering experiments on solutions having 99.4% (v/v), (pure d-cyclohexane from Cambridge Isotopes), 56.4%, 24.0% and 17.8% deuterated solvent. By varying the composition of the solvent, we hoped to elucidate both the insoluble d-PMMA core dimensions as well as the structural behavior of the PS arms comprising the corona.</p> <p>While these experiments were not of sufficient resolution to glean information about detailed structure of the micellar corona, interesting dimensional information can be extracted from our results. We first subtracted the background signal from our data by plotting $I \cdot q^3$ against q^3 according to a Porod analysis (4). The slope from this plot revealed background contributions to our scattering signal of 0.0044, 0.015, 0.0045 and 0.018 for the 99.4%, 56.4%, 24.0% and 17.8% d-cyclohexane solutions respectively. We then compared the scattering signal to that predicted from a structure with a core-shell morphology where we vary only the contrast between the core, shell and solvent with these experiments. This analysis provides us with a picture of our micellar dimensions where the core is 11 nm in radius and the</p>		

Experiment report (continued):

micelle is 46 nm in radius. The fits to this model are shown in Figures 1 and 2 below. In this analysis we require the core to be a dense sphere filled completely with d-PMMA, giving us an aggregation number for the micelles of 70 chains/micelle. The shell has an average volume fraction of 0.016 to conform to these dimensions. We note a satisfactory fit with this model but note that the details of the scattering pattern, i.e. the oscillations expected in the scattering from a sphere, are not resolved in these experiments. Subsequent studies have been revealing these details. We also are unable to elucidate the star-like nature of these micelles, as has been seen in our small angle x-ray scattering studies. We plan future experiments with selectively deuterated micelles to further investigate these structural features.

The information we have obtained on these micelles provides valuable guidance for our current studies of concentrated suspensions of such aggregates. The micelles appear to be extremely monodisperse and, having a glassy core, are resilient to concentration without changing their structure. This is the direction of our current efforts.

Figure 1 Logarithmic plot of intensity versus scattering vector q for PS-dPMMA solutions in 18 and 24% d-cyclohexane. The line is the result of a core-shell model with $R_c=11\text{nm}$ and $R_m=46\text{nm}$.

Figure 2 Logarithmic plot of intensity versus scattering vector q for PS-dPMMA solutions in 56.4% d-cyclohexane. The line is the result of a core-shell model with $R_c=11\text{nm}$ and $R_m=46\text{nm}$.

References:

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Instrument used: <i>(please type)</i> Low q Diffractometer	Local contact: P. Seeger R. Hjelm	Proposal number: <i>(for LANSCE use only)</i> 3343
Title: Tacticity Effects on the Miscibility of Polymer Blends		Report received: <i>(for LANSCE use only)</i> 3/12/91
Authors and affiliations: Greg Beaucage, R. S. Stein Department of Polymer Science and Engineering University of Massachusetts Amherst, MA 01003		
Experiment report: <p>PVME varying in triad-tacticity has been synthesized in our lab. The materials have been characterized using NMR, DSC, X-ray and GPC. Optical cloud point curves have been determined for blends with PS. Isotactic PVME crystallizes to a limited extent. In miscible blends with PS above the melting point of i-PVME a reduction in miscibility of about 10°C has been observed (for both deuterated and hydrogenated PS) in blends of similar molecular weights. Thus, a tacticity effect is defined¹.</p> <p>Small angle neutron scattering is the most accurate technique for the determination of χ for partially miscible polymer blends²⁻⁴. Using the data collected at LANSCE (8/90), RPA theory was used to fit neutron scattering patterns resulting in χ_{sc}/v_0 and $\bar{b}^2/v_0$ values as fitting parameters, where χ_{sc} is the interaction parameter (as measured in a scattering experiment) and $\bar{b}$ is a weighted mean statistical segment length. $\bar{b}^2/v_0$ for the isotactic blends showed strong temperature and composition dependences which were absent in the atactic blends. This behavior was accounted for in terms of i-PVME/i-PVME self-correlations. These correlations have been thermodynamically related to the equilibrium PVME melting point. Functional extrapolations of $b_{isotactic}$ PVME in the vicinity of the crystalline melting point have resulted in an estimated equilibrium melting point which agrees with measured values and predictions of melting point depression for the i-PVME/PS blends⁷. All SANS measurements were made above</p>		

Experiment report (continued):

what is believed to be the equilibrium melting point of 72°C and in blends whose composition completely inhibits crystallization.

The measured χ_{sc}/v_0 data was fit to the Flory-Huggins-Staverman (F-H-S) theory as developed by Koningsveld⁶. This fit generates four parameters, two of which are entropic in nature (non-combinatorial entropy terms), one enthalpic and an interacting unit surface area term, the Staverman parameter. In comparing these terms from atactic and isotactic blends it was found that the enthalpic term scales with the surface area term indicating that for similar blends which differ only in geometric factors (such as tacticity) changes in the enthalpy can be directly related to changes in the surface areas of the interacting units. The entropic term was shown to scale with the volume of the interacting units. Since volume changes twice as much as surface area the entropic changes in the F-H-S parameters dominate and miscibility is reduced for the isotactic blends. Thus, the final result of the SANS data is the conclusion that the tacticity effect is grounded in geometric factors.

Using the F-H-S equation for χ determined from the SANS data predictions were made into the immiscible regime in order to estimate the thermodynamic driving force for phase separation (i.e. to predict phase separation kinetics). This prediction agreed with experimental measurements of phase separation kinetics and with predictions made using F-H-S fits to optical cloud point data. Extrapolations in the opposite direction indicated anomalous behavior of χ at the equilibrium melting point of 72°C.

The understanding of this behavior gives a direct understanding of the factors effecting polymer-polymer miscibility and a direct relationship between an experimentally controllable parameter (tacticity) and the χ -parameter. Such understanding is useful in the *ab initio* prediction of miscibility in polymer-polymer blends.

References:

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- (5) S. Yang, R. S. Stein, *Macromolecules* **19**, 1667 (1986)
- (6) G. Beaucage, PhD Dissertation 3/91, U. Massachusetts, Amherst MA
- (7) P. J. Flory, *J. Chem. Phys.* **17**(3), 223-240 (1949).

Instrument used: (please type) LQD	Local contact: Phil Seeger	Proposal number: (for LANSCE use only) 3348
Title: Structure of Molecular Composites		Report received: (for LANSCE use only) 6/6/91
Authors and affiliations: D. W. Schaefer, B. J. Olivier, D. Loy and L. Gilliom Sandia National Laboratories Albuquerque, NM 87185 David McCarthy and James E. Mark Dept. of Chemistry University of Cincinnati Cincinnati, OH 45221		

Experiment report:

Three nanoscale phase-separated polymer systems were studied. All the materials combined a soft (organic or rubbery) and hard (inorganic or glassy organic) phases in an attempt to achieve increased toughness without loss of either modulus or elasticity. The SANS data demonstrate that a variety of structures arise in these complex *in-situ* filled nanocomposites.

Fig 1 shows LQD data for catalytically modified 1-2 polybutadiene. These materials are made by partially deuterating polybutadiene to produce glassy polyethylene. The data demonstrate deuteration is not random. Rather, correlated glassy domains are formed leading to a nanocomposite. Fig. 1 compares the unmodified material with a foam and bulk form of partially the deuterated composite. The data indicate that the domains are smaller in the bulk material and that the scattering from the foam porosity is comparable to that from the domains in the region below $.05\text{\AA}^{-1}$.

Fig. 2 shows the data for silica and titania filled polydimethyl siloxane. The data demonstrate domain formation in both the silica and titania filled materials, but complete dispersal of the filler for the combined silica/titania system. These latter materials are optically clear for all filler contents studied. The data also show that equal dispersion is obtained with both direct addition and *in-situ* generation of the water.

Fig. 1. Comparison of bulk and foamed forms of catalytically modified polybutadiene

Experiment report (continued):

Fig. 2. Comparison of silica/titania filled PDMS with each filler alone. Water of hydrolysis was added directly or generated *in-situ*.

Fig 3 shows the reduced scattering curves for a series of organically modified silica xerogels. Monomers of the form $\text{Si}_n\text{-PH}_m$ were synthesized where Si is silica and PH is a benzene ring. The data demonstrate small scale domains whose size increases with silica content. Comparable pure silicate material would have a Guinier radius of about 100Å. The data also indicate that the are polymeric structures as opposed to particulate colloidal structures. The unmodified data show considerable Porod-like scattering below .01Å⁻¹ (not shown) which we attribute to porosity.

The cold moderator was unavailable the experiment leading to some difficulty associated with lack of long wavelength neutrons and dead time corrections are large Q.

Fig. 3. Comparison of scattering data for three organically modified xerogels with different silica to organic ratio.

References:

Instrument used: <i>(please type)</i> LQD	Local contact: Rex Hjelm	Proposal number: <i>(for LANSCE use only)</i> 3361.0
Title: Small-angle neutron scattering investigation of ternary liquid crystalline phases.		Report received: <i>(for LANSCE use only)</i> 2/7/91
Authors and affiliations: Structural features of the cubic phase of a ternary surfactant system S. Radiman ¹ , C. Toprakcioglu ^{1,2} , L. Dai ¹ , A.R. Faruqi ³ , R.P. Hjelm Jr ⁴ and A. de Vallera ⁵ 1) Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K. 2) AFRC Institute of Food Research, Colney Lane, Norwich NR4 7UA, U.K. 3) MRC Laboratory of Molecular Biology, Hills Road, Cambridge CB2 2QH, U.K. 4) LANSCE, Los Alamos National Laboratory, Los Alamos, N.M. 87545, U.S.A. 5) Department of Physics, University of Lisbon, 1700 Lisbon, Portugal.		
Experiment report: <p>Abstract - We have studied the cubic phase formed by the ternary system water/didodecyldimethylammonium bromide/octane using small-angle x-ray and neutron scattering. We have observed the existence of more than one symmetry in this cubic region, with a transition from primitive to body centred cubic symmetry on increasing the water content of the system. Our results are consistent with a bicontinuous periodic structure of constant mean curvature. We also report rheological measurements which indicate that the ringing behaviour of the cubic samples is associated with a sharp increase in the quality factor as audible frequencies are approached.</p> <p>The above paper was published in Journal de Physique (Colloque C7), <u>51</u>, 375, 1990</p>		

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
LQD	P. A. Seeger	3365

Title:	Report received: (for LANSCE use only)
NEUTRON RESONANCE SCATTERING FROM $^{240}\text{Pu} \cdot \text{CALMODULIN}$	3/6/91

Authors and affiliations:

Trewhella, J., Rokop, S. E., Henderson, S., Life Sciences Division, Los Alamos National Laboratory.

Hobart, D., Palmer, P., Isotope and Nuclear Chemistry Division, Los Alamos National Laboratory.

Seeger, P. A., P-LANSCE, Los Alamos National Laboratory.

Experiment report:

BACKGROUND: The calcium ion is the major regulator of intra-cellular processes that occur on millisecond time scales. Regulation is generally achieved by Ca^{2+} binding to a protein and inducing a conformational change which allows the protein to activate a target enzyme. Calmodulin (CaM) is a ubiquitous Ca^{2+} binding protein known to regulate a wide variety of processes from neurotransmitter release to muscle contraction. We have been studying the solution structure of CaM as a free monomer in solution, and when it is interacting with target enzymes. Small-angle X-ray scattering data from CaM as a free monomer in solution do not agree well with its crystal structure. The crystal structure of CaM is unusual in that it shows two compact globular domains connected by an extended α -helix of about 9 turns, that is mostly exposed to solvent (Babu et al., 1985). There are two Ca^{2+} -binding sites in each globular domain. We have proposed an alternative model based on the solution scattering data (Heidorn and Trewhella, 1988). Our model preserves the structures of the two globular domains seen in the crystal form, but places them closer together, on average, by about 10 Å. This rearrangement requires flexibility in the interconnecting helix region. Small-angle neutron scattering data from CaM complexed with its binding domain from one of its target enzymes, myosin light chain kinase, support the idea that the interconnecting helix is flexible (Heidorn et al., 1989). These studies show that CaM adopts a much more compact structure when it binds the target enzyme domain. While there is a considerable body of indirect evidence to support the conclusions drawn from the small-angle scattering studies, the precise nature of the solution structure of CaM remains controversial. There are a large number of conflicting spectroscopic studies aimed at measuring the distance between the 4 Ca^{2+} -binding sites of CaM. If these distances were known, it would place important constraints on models for the structure in solution.

APPROACH: We have previously used neutron resonance scattering from the strong nuclear resonance in ^{240}Pu at 0.278 Å to measure the distances between ion-binding sites in CaM. Pu^{3+} has the same ionic radius as Ca^{2+} , and we were successful in stabilizing Pu^{3+} in a Tris buffer at pH 6 for several hours. We also established, using visible spectroscopy, that Pu^{3+} binds to CaM at 4 specific sites. Finally, we have shown that $4\text{Pu}^{3+} \cdot \text{CaM}$ activates one of its target enzymes (myosin light chain kinase) at least as efficiently as does $4\text{Ca}^{2+} \cdot \text{CaM}$, indicating that structural data derived from $4\text{Pu}^{3+} \cdot \text{CaM}$ is relevant to the biologically active form of CaM. Neutron data were collected from D_2O solutions of $4^{240}\text{Pu}^{3+} \cdot \text{CaM}$, $4\text{Ca}^{2+} \cdot \text{CaM}$, as well as a D_2O buffer. Each

Experiment report (continued):

of the CaM containing samples was approx. 50 mg/ml protein and the solution conditions were those for which CaM is known to be a soluble monomer. Resonance scattering from the ^{240}Pu in the ($4^{240}\text{Pu} \cdot \text{CaM}$ - buffer) data was observed (LANSCE experimental report #223), but the quality of the data were such that it was not possible to extract all the distances between ion-binding sites. During the 1990 run the liquid hydrogen moderator went down and we therefore had increased flux in the short wavelength regime needed for this experiment. We therefore decided to repeat the measurements (rather than the originally accepted proposal, which required long-wavelength neutrons) in the hope of obtaining significantly improved statistics on the data.

RESULTS: Data were again collected from D_2O solutions of $4^{240}\text{Pu}^{3+} \cdot \text{CaM}$, $4\text{Ca}^{2+} \cdot \text{CaM}$, as well as a D_2O buffer. Parameters of the ^{240}Pu resonance at $0.278 \text{ \AA}$ have been fitted (Lynn, 1991) to existing nuclear data using a generalized single-level formalism (Lynn & Seeger, 1990). This allows a precise computation of the wavelength-dependent sample transmission, and the real and imaginary parts of the scattering amplitude. Transmitted beam flux was measured using the ^6Li -glass scintillator chip in the beam stop, corrected for increased efficiency compared to the main detector and shifted in time to account for the slightly shorter flight path and the faster response. The observed transmission dip is in excellent agreement with theory. After subtracting the buffer scattering from that of the solution containing $^{240}\text{Pu} \cdot \text{CaM}$, a residual error exists because sample-independent background has been divided by a transmission function with a dip in it; this is corrected by subtracting a suitably normalized (Seeger & Hjelm, 1991) contribution from a run in which the beam was blocked by 15.3 mm of BN. Data from 24 time slices (λ between 0.261 and $0.294 \text{ \AA}$) were placed in 33 Q-bins, $0.1125 \text{ \AA}^{-1} \leq Q \leq 1.350 \text{ \AA}^{-1}$, and the wavelength-dependent data at each Q were then least-squares fitted to the form

$$I_{00}(Q) + \text{Re}\{b(\lambda)\} I_{0r} + |b(\lambda)|^2 I_{rr}(Q),$$

where a subscript r represents resonant and 0 represents non-resonant scattering. Within statistical uncertainties, $I_{00}(Q)$ and $I_{0r}(Q)$ were found to be constants, which were subsequently subtracted from the data to give Fig. 1. The individual values of $I_{rr}(Q)$ were again extracted, and are shown in Fig. 2. Error bars are statistics propagated through the entire data reduction procedure. Least-squares fitting of the function $1 + \sin(Qd)/Qd$ between $0.4 \text{ \AA}^{-1}$ and $1.0 \text{ \AA}^{-1}$ gives a point-separation distance d between 9.6 and $10.0 \text{ \AA}$. The minimum near $0.2 \text{ \AA}^{-1}$, taken by itself, yields a distance of approximately $51 \text{ \AA}$. More detailed model fitting is necessary before any confidence may be given to these values.

References:

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Heidorn, D. B., Seeger, P. A., Rokop, S. E., Blumenthal, D. K., Means, A. R., Crespi, H., & Trewhella, J., (1989) *Biochemistry* 28, 6757.
Trewhella, J. Heidorn D. B., & Seeger, P. A. (1990) *J. Mol. Cryst. and Liq. Cryst.*, 180A, 45.
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Seeger, P. A. & Hjelm, R. P., (1991) *J. Appl. Cryst.*, in press.

Figure 1.

Figure 2.

Instrument used: <i>(please type)</i> LOD	Local contact: P. A. Seeger	Proposal number: <i>(for LANSCE use only)</i> 3366
Title: DISTANCE BETWEEN THE ANTIGEN BINDING SITES OF DIFFERENT SUBCLASSES OF IgG MEASURED USING NEUTRON SCATTERING		Report received: <i>(for LANSCE use only)</i> 3/4/11
Authors and affiliations: T. R. Sosnick, P. A. Seeger and J. Trehwella, Los Alamos National Laboratory; D. C. Benjamin, University of Virginia; J. Novotny, SQUIBB Institute for Medical Research.		
Experiment report: <p>The most common antibody class is IgG, which is a 150 kD symmetrical Y or T shaped molecule with two identical antigen binding sites at the ends of the two arms. While there are high resolution crystallographic data on portions and fragments of IgG as well as hinge deleted IgG's, information about the complete structure of native IgG is lacking. Small-angle X-ray and neutron solution scattering studies have been done on IgG, but due to the inherent problems of spherical averaging, it has not been possible to determine unique structures. We have measured the distances between the antigen binding sites for 3 different IgG mouse monoclonal subclasses (IgG1, 2a and 2b) using neutron contrast matching from deuterated antigen (staphylococcal nuclease obtained using a bacterial expression system, grown in fully deuterated media) complexed with proteated IgG. We used a 41% D₂O solvent to contrast match the proteated antibody molecule. In order to account for any slight mismatch, we subtracted a background signal from proteated nuclease and IgG sample. The difference scattering signal is then primarily from the deuterated antigens. This gives rise to a profile that contains an interference term related to the distance between the antigens. If the antibody was rigid, then the oscillations in the interference term should be observed. This was not the case (Figure 1). The scattering profile has been modeled with a flexible antibody where the distance was variable (Figure 2). In this model, the average distance for all three subclasses is between 110 and 150 Å with the variance of this distance greater than 30 Å implying a highly flexible structure (Further data analysis in progress will allow us to better quantify these parameters.). This similarity was not anticipated because measurements using fluorescence polarization techniques (1) had shown differences in flexibility between the subclasses and this was correlated with the ability to activate the immune system. The common degree of flexibility of the two arms we observe might be a necessary requirement for bivalent antigen binding whereas the functional differences between the subclasses would appear to be related to the over-all flexibility and arrangement of the Y-shaped IgG molecule.</p>		

Experiment report (continued):

Figure 1

Figure 2

References:

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Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>																				
LQF	Dr. P. Seeger	3381																				
Title:		Report received: <i>(for LANSCE use only)</i>																				
The Structure of Polymers in Concentrated Dispersions		2/19/91																				
Authors and affiliations:																						
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Experiment report:																						
<p>Experimental</p> <p>This experiment concerned the adsorption of AB block copolymers of polystyrene/polyethylene oxide onto silica particles. The polymers have been previously studied using the Force Balance and their detailed structure is given in Table 1. The silica particles were obtained from Degussa and had a surface area of 320m²g⁻¹. The samples were dispersed in a medium of 15.8%D and 85.13%H toluene. This was found to accurately contrast match the silica particles though their stated density (2.2 g/cm³) would have suggested a higher deuterated component. The dispersions were made up at a solids concentration of ~ 6.8%.</p> <table border="1"> <thead> <tr> <th>Polymer</th> <th>M_w</th> <th>Polystyrene</th> <th>PEO</th> </tr> </thead> <tbody> <tr> <td>2/4</td> <td>384</td> <td>208</td> <td>176</td> </tr> <tr> <td>62/4</td> <td>6,624</td> <td>6,448</td> <td>176</td> </tr> <tr> <td>100/4</td> <td>10,576</td> <td>10,400</td> <td>176</td> </tr> <tr> <td>500/4</td> <td>52,176</td> <td>52,000</td> <td>176</td> </tr> </tbody> </table> <p>Results</p> <p>Although the contrast match for the samples was very good, with particles which are not entirely homogeneous there is always some residual scattering. In this instance it is essential to subtract the scattering from the bare particle. This is however not a trivial exercise, especially when the scattering from the</p>			Polymer	M _w	Polystyrene	PEO	2/4	384	208	176	62/4	6,624	6,448	176	100/4	10,576	10,400	176	500/4	52,176	52,000	176
Polymer	M _w	Polystyrene	PEO																			
2/4	384	208	176																			
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500/4	52,176	52,000	176																			

Experiment report (continued):

adsorbed layer is itself rather weak. To this end the scattering of each stable dispersion in say pure D-toluene could be used for the subtraction. However the data for these samples was rather poor and further analysis is necessary before this can be done. Further data as a function of contrast is necessary.

Figure 1 show the scattering normalized to the first data point for the range of samples at contrast match described in Table 1.

The scattering from the samples is rather erratic. One problem with the data is that in an attempt to maximize the scattering from the surface rather small particles were chosen. For the 2-4 and the 62-4 data this should not be problematic but for the 100 and 500 there will be a pronounced effect of curvature. Estimating the second moment [1] from these data and the overall radius of gyration gives some indication of the adsorbed layer thickness, though a more detailed treatment is required.

This simple analysis indicates a radius for 2-4 (including the particle) of 20 ± 2 nm. This should be close to the 'effective' bare particle radius. Trying to fit this data to a surface function shows that if a layer is present it is extremely thin, as expected. The sample 62-4 shows a much larger radius of gyration of 44 ± 2 suggesting that the 62-4 sample has an thickness ~ 15 nm. This is several times greater than the radius of gyration of 62 polystyrene segments - suggesting a very extended layer. The data for 100-4 and 500-4 show no change in thickness compared to 2-4 and with these samples there may have been some problems due to aggregation. Further work on these polymers is clearly indicated.

References:

- [1] I. Osgrrove, T.L. Crowley, T.G. Heath and K. Ryan *Macromolecules* [1989] 20 2879.

Instrument used: <i>(please type)</i> LQD-1	Local contact: Phil Seeger	Proposal number: <i>(for LANSCE use only)</i> <div style="border: 1px solid black; padding: 2px; display: inline-block;">3382</div>
Title: Neutron Scattering from Selectively Labeled Model Linear Low Density Polyethylene.		Report received: <i>(for LANSCE use only)</i> 6/10/91
Authors and affiliations: <p style="text-align: center;"> M. M. Satkowski⁺, S. D. Smith⁺, I. Noda⁺, and R. S. Stein[*] ⁺ The Procter & Gamble Company, Cincinnati, Ohio. [*] Polymer Research Institute, University of Massachusetts, </p>		
Experiment report: <p> The small angle neutron scattering of selectively deuterated short chain branched (SCB) polyethylenes were measured. These polymers were synthesized by copolymerization of deuterated octene and hydrogenous ethylene in varying proportions (2-7 mole %). The object of the experiment was to compare small angle neutron and x-ray scattering in order to determine if the deuterium labelled short chain branches were preferentially located at the crystal/amorphous interface. It has been speculated that this type of branch location produces mechanical property differences found among linear low density polyethylenes (commercial copolymers of ethylene and either octene or butene) that cannot be accounted for by changes in amount of crystalline material alone.¹ Based on thermodynamic considerations, Mattice et al. have predicted such branch enhancement at the crystal surface.^{2,3} </p> <p> A comparison of the SAXS and SANS for one level of branching. show that for the quickly cooled (ca. 80°C/min) patterns do not show any significant differences in periodicity (see Figure 1). The SAXS patterns were obtained at Oak Ridge National Laboratory in collaboration with J. S. Lin. The interfacial boundary thicknesses determined using a Porod type analysis⁴ are also very similar. This would indicate that the SCB are excluded from the crystalline region and are distributed more or less evenly throughout the amorphous regions. Slowly cooled samples (ca. 1°C/min) show differences in interfacial widths, but the uncertainty in the SANS background corrections (high incoherent scattering) make quantitative estimates difficult. Also, some detector saturation during </p>		

Experiment report (continued):

transmission measurements (caused by the increase in beam current during the experimental run) contributed to uncertainty in relative intensity values. We are calculating scattering from model lamellar distributions and interfaces and attempting to account for the obtained patterns, using predictions by Mattice² of how many branch units could be accumulated near the amorphous/crystalline boundary as an upper bound.

Figure 1. SANS and SAXS of d-octene/ethylene copolymer , 4 mole% branching. Crystallization conditions : Quenched from melt (160°C) to 0°C.

References:

- ¹Speed, S., *Plastic Eng.* **28**, July, 29 (1982).
- ²Mattice, W., and Saubhagya, M., *Macromolecules*, **20**, 155 (1988)
- ³Mathur, S., and Mattice, W. , *Macromolecules*, **21**, 1354 (1988).
- ⁴Vonk, C. in *Small Angle X-ray Scattering* Glatter, W. and Kratky, O eds., Academic Press, New York (1982).

Instrument used: (please type) LQD	Local contact: Rex Hjelm	Proposal number: <i>(for LANSCE use only)</i> 3374
Title: Neutron Scatter Studies of Nucleosome and Chromatin Structures Related to Biological Functions.		Report received: <i>(for LANSCE use only)</i>
Authors and affiliations: E.M. Bradbury - U.C. Davis/LANL Brian Imai - Life Sciences Division Peter Yau - U. C. Davis Gary Schroth - U. C. Davis Jill Trewhella - Life Sciences Division Tobin Sosnick - Life Sciences Division Rex Hjelm - P-LANSCE		
Experiment report: Due to the failure of the hydrogen moderator on the LQD instrument our time was given up to other investigators. No experiments were performed.		

Instrument used: (please type) LQD	Local contact:	Proposal number: (for LANSCE use only) 3386.5
Title: Critical Phenomena in Binary Mixtures in Confined Geometries		Report received: (for LANSCE use only) 3/4/91
Authors and affiliations: P. Wiltzius, AT&T Bell Laboratories, Rm 1C-352, 600 Mountain Ave. Murray Hill, NJ 07974 S. B. Dierker, Department of Physics, University of Michigan, Ann Arbor, MI 48109		
Experiment report: <p>During this year's run we continued the investigation of critical phenomena of binary liquid mixtures in restricted geometries using SANS. Previously we focused mostly on mixtures of water and lutidine imbibed into porous VYCOR glass which has an interconnected internal void space with geometric and chemical randomness. This glass-liquid system is thus ideally suited for the study of the random field transition (1-3). Motivated by our experiments A. Liu and coworkers (4) have worked on the theory of wetting phenomena in restricted geometries. For reasons of simplicity they concentrated on straight cylindrical pores, which are the simplest possible geometrical form for the confinement. It is well known (5) that for a two-component fluid mixture near its critical point which is in contact with a glass wall one of the fluid phases completely wets the glass. It has thus been speculated that wetting phenomena play an important role for binary fluids imbibed in porous glasses. Liu et al. have predicted novel transitions in cylindrical pores of sufficiently small radius r_0 as the fluid mixture is taken deeper into the two-phase region away from the critical point. Fig. 1 shows the predicted wetting phase diagram for a binary liquid mixture confined in a cylindrical pore as a function of reduced temperature t and inverse pore radius, a/r_0, where a is a molecular length. The sizes of the wetting layers, tubes, capsules and plugs as a function of temperature and time should be measurable using SANS, in particular since contrast matching should allow us to suppress the large uninteresting scattering signal expected from a system of tubes. Interestingly, theory (4) predicts that capsules should show metastability similar to what we observed for the randomly structured porous Vycor (1-3) and interpreted as evidence for a random field transition. Comparing the behavior of critical fluid mixtures confined in simple geometries to that observed for Vycor should shed light on differentiating between the effects of confinement and randomness, respectively. We thus performed experiments using Anotec membranes, which consist of tubular channels in a honey-comb structure. The critical mixture of choice remained the well-studied and characterized mixture of (water/heavy water) and lutidine.</p> <p>In a first set of experiments we measured the structure factor of the dry membranes. Fig. 2 shows a radially averaged $S(q)$ of the scattering by one 60 μm thick membrane. To our big surprise</p>		

Experiment report (continued):

we measured a huge number of neutrons scattered at $q \leq 0.01 \text{ \AA}^{-1}$. As a comparison we note that the scattering by a 1 mm thick piece of dry Vycor is only on the order of 100 in the same units. Tilting the membrane at an angle of 45° with respect to the incoming beam yields a 2-dimensional $S(q)$ as shown in Fig. 3. We think that this and other similar $S(q)$ are due to total internal reflection of neutrons by the pore walls. *Anotec* is made of aluminum oxide, which has a calculated scattering length density $\rho = 4.5 \times 10^{10} \text{ cm}^{-2}$. The angle of total internal reflection θ_0 for neutrons of wavelength λ and the corresponding wavevector of total internal reflection q_0 are given by

$$\sin \theta_0 \approx \lambda \sqrt{\rho / \pi} \qquad q_0 \approx 2 \sqrt{\pi \rho} \approx 7.5 \times 10^{-3} \text{ \AA}^{-1}$$

This means that neutrons glancing off of the pore walls at angles corresponding to wavevectors smaller than q_0 are totally reflected and have a chance to miss the beam stop, hence giving rise to the remarkable forward scattering measured on the detector. The solid line in Fig. 2 is a fit to the expected reflectivity close to glancing incidence

$$R = \left\{ \frac{1 - [1 - a]^{1/2}}{1 + [1 - a]^{1/2}} \right\}^2 \qquad \text{with } a = (\theta_0 / \theta)^2.$$

We added a small background of 1.85×10^{-3} to R .

In a next set of experiments we determined the scattering length density of *Anotec*. We imbibed various mixtures of H_2O and D_2O into the membranes and measured $S(q)$. Fig. 4 shows the results for five different mixtures. The overall forward scattering could be greatly reduced (roughly three orders of magnitude at $q = 0.01 \text{ \AA}^{-1}$) for mixtures with $\rho \approx 4.4 \times 10^{10} \text{ cm}^{-2}$. This scattering length density is very close to the calculated ρ for aluminum oxide. Unfortunately the residual scattering in the forward direction is highly sensitive to the composition of the fluid mixture. A change by a few percent in composition changes the scattering by factors of 5, forecasting difficult data analysis for the critical mixtures.

We prepared a critical fluid mixture with $\rho = 4.38 \times 10^{10} \text{ cm}^{-2}$ and imbibed it into the *Anotec* membrane. We measured the temperature dependence of the scattering and are currently working on the quantitative analysis of the data.

References:

- (1) S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. 58, 1865 (1987).
- (2) P. Wiltzius, S. B. Dierker, and B. S. Dennis, Phys. Rev. Lett. 62, 804 (1989).
- (3) S. B. Dierker and P. Wiltzius, Phys. Rev. Lett. 66, 1185 (1991), and Proceedings of the Materials Research Society, Fall Meeting in Boston 1989.
- (4) A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. 65, 1897 (1990).
- (5) J. W. Cahn, J. Chem. Phys. 66, 3667 (1977).

Experiment report (continued):

Figure 1

Figure 2

Figure 3

Figure 4

References:

Instrument used: (please type) LQD	Local contact: Dr. P.A. Seeger	Proposal number: (for LANSCE use only) 3393.0
Title: CHARACTERIZATION OF POLYMER MOLECULES AT INTERFACES BY SMALL-ANGLE NEUTRON SCATTERING		Report received: (for LANSCE use only) 1/30/91
Authors and affiliations: W.C. Forsman and B.E. Latshaw 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 (1) examine the conformation of polymer molecules confined to the solid-liquid interface in dispersions of finely divided particles, and (2) to determine the coverage of the particles in mass of polymer per unit of interfacial area.* 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 a particle ($Z=0$) out into the continuum dispersant.</p> <p>The systems studied in this first experiment consisted of samples of narrow molecular weight distribution poly(n-butyl methacrylate) with molecular weights of 45000 and 7000 g/mol that were chemically bonded (grafted) by one chain-end to nearly monodisperse, 2300 Å SiO_2 spheres. Both bare spheres and spheres with grafted polymer were dispersed in isopropanol (IPA). Experiments were done in mixtures of hydrogenous and deuterated IPA -- (HIPA and DIPA respectively). dispersions were prepared with 100, 80, 60, 40, 20 and 0.0% DIPA.</p> <p>In a SANS experiment, scattering from bare 2300 Å spheres are in the asymptotic regime (scattered intensity dropping off as Q^{-4}). We had thus expected the difference in scattering between bare SiO_2 particles and particles with grafted polymer to be relatively easily interpreted in terms of the coverage of polymer and its conformation.</p> <p>As it turns out, our scattering results indicated that the SiO_2 spheres had considerable structure which had to be considered when analyzing data from scattering of spheres with grafted polymer. First, the particles had a random density fluctuation over a length scale of about 7 Å. Secondly, scattering indicated that the "bare" particles were, in fact, covered with a relatively uniform layer about 45 Å thick. According to the scattering length density of the layer and the known chemical properties of SiO_2, we interpreted the layer as being a "spongy", highly hydrolyzed material, probably containing sorbed dispersant.</p> <p>The complexity of the particle structure posed no serious difficulty in interpretation of the scattered intensity of the grafted particles. We found, however, that the process of grafting the polymer to the surface of the particles actually changed the surface composition of the particles themselves. Indeed we found the presence of a layer of hydrocarbon, (probably butyl) overlaying the</p>		
<hr/> <p>*The polymer coverage can, of course, be determined by a number of chemical methods. SANS would not be considered for that application alone. But it is important to calculate coverage from the scattering results as a check on the suitability of the small-angle neutron scattering for characterization of this class of systems.</p>		

Experiment report (continued):

SiO₂. It was probably bound to the silica surface by transesterification during the grafting reaction.

We were pleased that the scattering experiments gave polymer coverage close to the values determined independently in the laboratory. This indicates that the SANS technique is a sound one for "looking at" polymer molecules confined to solid-liquid interfaces in dispersions of finely divided particles.

After taking into consideration the particle structure, there was no special difficulty in modeling the results of the scattering experiments in terms of $\phi(Z)$. Results were presented at the most recent national meeting of the AIChE.⁽¹⁾

One of the interesting findings, the effect of molecular weight on $\phi(Z)$, is illustrated below. Scattered intensities and model predictions are shown, along with the associated $\phi(Z)$ for polymers of molecular weights of 45,000 and 7,000 g/mol in 100% DIPA. We note that the segments of the lower MW sample are extended further out into the continuum dispersant than those of the higher MW sample. This is true even though the unperturbed root-mean-square radius of gyration of the higher molecular weight sample is approximately 2.5 times that of the lower MW sample. This can be explained by the fact that the surface coverage of the lower MW sample is twice that of the higher.* Higher coverage leads to crowding, and forces the chains near the surface into extended conformations. One could thus describe the conformation of the lower MW sample as brushlike,⁽²⁾ at least for repeat units near the surface.⁽³⁾

DIFFERENCE SCATTERING BETWEEN
GRAFTED AND BARE SILICA PARTICLES

MW = 45,000 g/mol 100% DIPA

DIFFERENCE SCATTERING BETWEEN
GRAFTED AND BARE SILICA PARTICLES

MW = 7,000 g/mol 100% DIPA

POLYMER DENSITY PROFILE

MW = 45,000 g/mol 100% DIPA
Coverage = 3.2×10^{-7} g/cm²

POLYMER DENSITY PROFILE

MW = 7,000 g/mol 100% DIPA
Coverage = 6.0×10^{-7} g/cm²

References:

1. B.E. Latshaw and W.C. Forsman, National Meeting of the American Institute of Chemical Engineers, Chicago, Illinois, November 12, 1990.
2. This phenomenon has been described theoretically: S.T. Milner, T.A. Witten and M.E. Cates, *Macromolecules*, 21, 2610 (1989).
3. Papers covering the results of these experiments are now in preparation.

*Anchor points of the grafted chains for the lower MW sample are an average of 14 Å apart, whereas for the higher MW sample they are an average of 48 Å apart.

Instrument used: (please type)LQD	Local contact: R. Hjelm/ P. Seeger	Proposal number: (for LANSCE use only) 3397
Title: Inelastic Scattering Effects in TOF SANS		Report received: (for LANSCE use only) 3/1/11
Authors and affiliations: <u>Rex P. Hjelm, Jr.</u> LANSCE Phil Seeger LANSCE P. Thiyagarajan IPNS Division, Argonne National Laboratory		
Experiment report (continued): <p>The measurements described here partially covered one aspect of the proposal to evaluate inelastic effects in TOF-SANS measurements, namely to evaluate the importance of such effects in samples of known size and structure in different mixtures of H₂O and D₂O. There was insufficient discretionary time to carry out the remainder of the program.</p> <p>EXPERIMENTAL: Colloidal silica gel, HS-30, stated by the manufacturers to be spherical particles and to be of well characterized size, 120Å, where used in these measurements. The silica gel content is 30% in the stock solutions. Samples were prepared by diluting stock solutions to 3% W/V. Care was taken with pH and NaCl concentration to stabilize the solutions. Samples were made in 100%, 80%, 60% 40%, 20% and 0% D₂O. Discretionary time allowed only measurements with the LH₂ moderator with the MgO filter in and the H₂O moderator with the MgO filter out.</p> <p>RESULTS: Scattering curves taken with the liquid hydrogen moderator were measured for each sample between $Q \approx 0.003$ and $0.2 \text{ \AA}^{-1}$. Those obtained using the ambient water moderator covered the range $0.006 < Q < 0.5 \text{ \AA}^{-1}$. Two complete contrast series were obtained. The analysis is far from complete, but initial indications show systematic differences in $d\Sigma/d\Omega$ for Q less than $0.01 \text{ \AA}^{-1}$, and greater than $0.05 \text{ \AA}^{-1}$. We have not yet reached any conclusion as to the sources of these differences.</p>		

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
LQD	Phil Seeger	3415
Title:		Report received: <i>(for LANSCE use only)</i>
Rod-like Structure in Shear-Oriented Mixed Colloids		5-31-91
Authors and affiliations:		
Rex Hjelm (LANSCE)		
Experiment report:		
<p><i>This experiment was attempted but no readable results were obtained because the shear cell failed.</i></p>		

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
LQD	Phil Seeger	3425
Title:		Report received: <i>(for LANSCE use only)</i>
COMPRESSIBILITY OF POWDERS II		6/13/91
Authors and affiliations:		
<p>ALAN J. HURD^{1,2}, GREGORY P. JOHNSTON², DOUGLAS M. SMITH², and P. A. SEEGER³</p> <p>¹Sandia National Laboratories, Albuquerque, New Mexico 87185-5800 (USA),</p> <p>²Center for MicroEngineered Ceramics, University of New Mexico, Albuquerque, New Mexico 87131 (USA)</p> <p>³Los Alamos National Laboratory, Los Alamos, New Mexico 87545 (USA)</p>		
Experiment report:		
<p>ABSTRACT</p> <p>Previous studies of fumed silica by mercury porosimetry (ref. 1) established an inverse dependence of the powder compressibility κ on applied pressure P, heralded by power-law differential volume vs pressure curves; this law was confirmed by independent mechanical compressibility measurements (ref. 2).</p> <p>Preliminary small-angle neutron scattering (SANS) suggested that the zero-angle intensity $I(q \rightarrow 0)$ is proportional to the compressibility κ, possibly mimicing systems in thermodynamic equilibrium. In this study, we have tested this relationship, in both the low and high pressure regimes, by correlating the scattered neutron intensity from samples in various degrees of compaction. We find that, while the intensity does decrease with increasing compaction (after removing the effects due merely to greater sample density) as expected according to the compressibility analogy, the dependence is not the same as that found by mercury porosimetry. This report is an extension of one given previously (ref. 3).</p>		
<p>INTRODUCTION</p> <p>Previous studies (refs. 1,2) of fumed silica compaction yielded an empirical "equation of state" between powder pore volume V_p and applied pressure P,</p>		
$V_p \propto P^{-1/3}. \quad (1)$		
<p>The compressibility, which is defined as</p>		
$\kappa \equiv - \frac{1}{V} \frac{dV}{dP} = - \frac{1}{V} \frac{dV}{dP} P, \quad (2)$		

Experiment report (continued):

is therefore inversely proportional to pressure. Here V , the total volume of the powder, is comprised of compressible pore volume V_p and incompressible silica volume V_s : $V=V_p+V_s$.

Preliminary scattering studies on compacted fumed silica powders demonstrated that $I(0)$ decreases with increasing compression. In this study we attempt to test the relationship

$$I(0) \propto \kappa^? , \quad (3)$$

which would imply a straightforward statistical understanding of Eq. (1).

Using $\kappa \propto 1/P$ from Eqs. (1) and (2), we would expect

$$I(0) \propto P^{-1} \propto V_p^3$$

Instead we observe³ (for $V_p/V_s < 10$)

$$I(0) \propto V_p^\nu \quad \nu = 1.25 \pm 0.25 \quad (10)$$

The exponent is somewhat larger than that estimated earlier ($\nu = 0.75$) from sparse data (ref. 3).

We conclude that Eq. (3) does not hold for our powder samples. The failure of Eq. (3) does not mean that it has no ergodic⁴ analog for fumed silica powder, but merely that the large scale fluctuations measured by $I(0)$ do not control the compressibility in the same way as in thermal systems.

References:

- 1 D. M. Smith, G. P. Johnston, and A. J. Hurd, J. Colloid Interface Sci., in press.
- 2 F. Ehrburger and J. Lahaye, J. Phys. France 50, (1989) 1349.
- 3 A. J. Hurd, G. P. Johnston, and D. M. Smith, "Characterization of Porous Solids II," edited by F. Rodriguez-Reinoso, in press.
- 4 S. F. Edwards and R.B.S. Oakeshott, Physica D 38, (1989) 88.

Instrument used: (please type) LQD	Local contact: Thomas Rieker / Rex Hjelm	Proposal number: (for LANSCE use only) 34310
Title: Structural Study of Highly Fluorinated Thermotropic Liquid Crystals by Small Angle Neutron Scattering		Report received: (for LANSCE use only)
<p>Authors and affiliations:</p> <p><u>Thomas Rieker</u>¹, Eugene Janulis², and Rex Hjelm¹</p> <p>¹Manuel Lujan Jr. Neutron Scattering Center (LANSCE), Los Alamos National Lab, Los Alamos, NM 87545</p> <p>² 3M Inc., Corporate Research Laboratories, St. Paul, MN 55144-1000</p>		
<p>Experiment report:</p> <p>Several unique families of highly fluorinated thermotropic liquid crystals have been developed at 3M Inc. for use in electro-optic devices. Observations made with polarized light microscopy revealed that these materials exhibit unusual textures in the liquid crystal phases in comparison to non-fluorinated materials. Since optical textures provide macroscopic evidence for microscopic ordering the 3M scientists proposed a new liquid crystalline structure. We have undertaken a collaboration with 3M to investigate the structures formed by highly fluorinated materials by small angle X-ray (SAXS) and neutron scattering (SANS).</p> <p>The 3M liquid crystals differ greatly from typical perhydro materials in that one of the two aliphatic tails is highly fluorinated. These molecule have two chemically, electronically and sterically different ends. In addition the fluorination provides for strong neutron contrast.</p> <p>The 3M chemists proposed an interdigitated smectic structure for which the interlayer spacing is approximately 1.4 times the molecular length with the fluorinated tails arranged as nearest neighbors at the smectic layer boundaries and the hydrogen tails interdigitated at the center. This model was based on their knowledge of the behavior of perfluorinated alkyl chains in hydrocarbon environments.</p> <p><u>Pure Materials:</u></p> <p>SANS experiments were conducted on the pure compounds; $C_{10}H_{21}-C_4H_2N_2-C_6H_4-O-CH_2-C_nF_{2n+1}$ where $n=3,5$, and 7, contained in standard 2 mm quartz cells. Data was collected for approximately one hour at a temperature which corresponded to the midpoint of each liquid crystalline phase. Figure 1 shows a typical radial average plot which demonstrates two important features general to all phases in these materials.</p> <ol style="list-style-type: none"> 1) A Bragg peak at approximately $Q = 0.2 \text{ \AA}^{-1}$ is evident. 2) This Bragg peak is unexpectedly weak for a pure ordered material with high scattering contrast. 		

Experiment report (continued):

Fig. 1, Intensity vs. Q (all time slices) for the smectic C phase (81 °C) of $C_{10}H_{21}-C_4H_2N_2-C_6H_4-O-CH_2-C_7F_{15}$

These results indicate that the pure fluorinated materials do not form the proposed interdigitated structure, but rather a typical smectic structure in which the interlayer spacing is comparable to the molecular length. The weakness of the Bragg peaks further suggest that the nearest neighbor tail groups within a layer alternate between hydrogenated and fluorinated tails.

Two other general features in the data are noted: 1) the structure below $Q = 0.04 \text{ \AA}^{-1}$ is an artifact which suggests that the blocked beam corrections needs to be adjusted, 2) the increase in intensity above $Q = 0.3 \text{ \AA}^{-1}$ is due to the incoherent background from the large amount of hydrogen in this system.

We intend to pursue our structural investigation of these materials through neutron and X-ray diffraction experiments and by structural modelling using the General Structure Analysis System (GSAS) program.

Solvated Materials:

The 3M researchers have found that the fluorinated materials form unusual gel-like phases at room temperature when diluted in a hydrocarbon solvents. We prepared 5.0% solutions of $C_mH_{2m+1}-O-C_6H_4-COO-C_6H_4-O-CH_2-C_7F_{15}$ where $m = 6$ and 10, in n-heptane. Standard 2 mm quartz cells were filled with the solutions and sealed. Data was collected for approximately one hour at room temperature.

Data for the $m = 10$ sample is shown in figure 2. Once again we note two features:

- 1) A Bragg peak is observed at approximately $Q = 1.2 \text{ \AA}^{-1}$.
- 2) The Bragg peak is again weak, but notably stronger than in the pure materials.

Experiment report:

Fig. 2, Intensity vs. Q (all time slices) for a 5.0% solution of $C_{10}H_{21}-O-C_6H_4-COO-C_6H_4-O-CH_2-C_7F_{15}$ in n-heptane at room temperature.

The observed Bragg peak indicates the formation of a periodic structure with a 51 Å spacing which corresponds to approximately 1.5 times the molecular length. We would expect the Bragg peak to be very weak in a dilute solution. The fact that the Bragg peak is stronger in this case than for the pure materials suggests that the fluorinated tails are aggregating. This agrees well with the model proposed by the 3M researchers. However, we have yet to separate out the dilution effects.

For the solvated liquid crystals we intend to investigate the effects of concentration on the resultant structure by X-ray scattering and appropriate modelling.

Instrument used: <i>(please type)</i> LQD	Local contact: Rex Hjelm	Proposal number: <i>(for LANSCE use only)</i> 901001
Title: Swelling of Sephadex chromatography gels		Report received: <i>(for LANSCE use only)</i> 3/1/91
Authors and affiliations: Scott R. Rudge, Howard J. M. Hanley, and Gerald C. Straty National Institute of Standards and Technology 325 Broadway Boulder, CO 80303-3328		
Experiment report: <p>The thermodynamics of swelling of polymer based chromatography resins are being studied. A description of gel swelling has been given by Flory that depends upon two parameters. The first, a polymer solvent interaction parameter χ_1, may be measured by light scattering. The second, ν_e, the total number of chains in the gel network, was hypothesized in this work to be accessible by neutron scattering. Understanding the partitioning of solvent into the resin phase is fundamental to understanding the partitioning of other solutes.</p> <p>Sephadex gels G-10 and G-100 were preswollen in D₂O for four days prior to being transferred via syringe to 2 mm banjo cells and sealed. Care was taken to ensure that Sephadex gel completely filled the banjo cell, and that excess D₂O at least partially filled the neck. Scattering measurements were made on these gels for 2 to 8 hours in the LQD SANS machine, until at least 10⁶ counts were recorded. The data were reduced with transmission data, and scattering and transmission on a pure D₂O sample.</p> <p>The data were plotted as $1/I$ vs. Q^2, with the slope being proportional to ξ, the Debye screening length in the gel. We assumed that this length was the same as the distance between crosslinks, and used this distance to calculate ν_e. A distance of 7 Å was used for the length of a monomer subunit in the polymer gel. The molecular weight of the anhydroglucose unit is 162 dal. The results of the calculation compared to experimentally observed swelling were good for Sephadex G-10, but not for G-100. We suspect that the chain correlation length for G-100 is beyond the resolution of the configuration used. Based on swelling data, this distance should be 600 Å. This work has been continued at the NIST facility in Gaithersburg for different grades of Sephadex.</p>		

Instrument used: (please type) LQD	Local contact: R.P. Hjelm	Proposal number: (for LANSCE use only) 901003
Title: LECITHIN-GLYCOCHOLATE MIXED MICELLES AS A DRUG DELIVERY SYSTEM: STRUCTURAL INFLUENCE OF TAXOL		Report received: (for LANSCE use only) 2/28/91
Authors and affiliations: Rex P. Hjelm, Jr (LANSCE), P. Thiyagarajan (IPNS), and Hayat Alkan (Dept of Pharmaceutics, Univ of Illinois)		
<p>Experiment report: Significance: We have been investigating the structure of particles form in mixed aqueous colloids of lecithin and the bile salt, glycocholate¹⁻³. This system is important applications in studies of the structure and action of bile in the transport of fatty material both in from the liver and in digestion. This system also has potential as a novel delivery system for insoluble drugs. This application relies on the fact that mixtures of bile salts and lecithin spontaneously form single bilayer vesicles on dilution¹⁻³. The vesicles then would be used as "liposomes" to carry the drug. How the presence of the drug might affect the spontaneous formation of vesicles is important in realizing this application. Small-angle neutron scattering (SANS) supplies information of the structure over length scales most relevant to this question. The hight contrast of the lipid particles in D₂O allows the system to be studied over a broad range of concentrations.</p> <p>For our first look at the structural issues associated with the use of lecithin bile salt mixed colloids as drug delivery systems we consider the compound taxol⁴ (I), derived from the stem bark of the western yew, <i>Taxus brevifolia</i>.. Taxol has potent antileukemic and tumor inhibitory properties, but its extreme aqueous insolubility has limited its therapeutic use. The importance of developing a method of solubilizing taxol is underscored by the fact that the NCI has issued a RFP to research an acceptable formulation. We have replied to this RFP, and this work is part of the preliminary assessment on the use of our colloid system in providing such a formulation. This work may establish SANS as an important tool in pharmaceutical research.</p> <p>Objective: The particle structures of these mixed colloids are highly sensitive to total lipid concentration. We want to determine the effects of taxol on the structural transitions which occur with dilution using taxol concentrations near envisioned for therapeutic use. The behavior of the system with dilution is particularly important, as the envisioned formulation would involve reconstitution of taxol in a concentrated mixture of lecithin and bile salt. This mixture would then be diluted to form liposomes for <i>intra venous</i> injection in a manner similar to that done here.</p> <p>Experimental: Control stock preparations of glycocholate and lecithin were made up in D₂O to 50 g/l total lipid, as described elsewhere¹. Taxol-containing solutions where made up in a similar manner but contained 70 μM taxol (0.07 mole % taxol to lipid). This load is near that expected in therapeutic applications. Solubilization of taxol is indicated by the lack of visible precipitation in the solutions. Dilutions where made of the control and taxol stock using D₂O buffer. Neutron scattering was done on LQD using the H₂O moderator at the end of cycle 58, during which 100 μA was scheduled.</p> <p>Results: Visual inspection of samples showed the controls and taxol-containing samples to be identical in appearance. The 3x-diluted samples are clear . Opalescence is evident in 7x-diluted samples. This increases to a maximum at 10x dilution, which is at the concentration for the onset of vesicle formation³. The samples are clear at 15x dilution. Only vesicles are found at this concentration. Only 5x, 7x and 9x controls and taxol-containing samples where measured due to poor beam availability. The results are shown in Figs 1-3. These represent the approach to the concentration dependent transition from rod-like to vesicle forms³. No differences are evident in the 5x dilution. Some differences are observed at low Q in the 7- and 9-fold diluted samples: the scattering intensities from taxol-containing samples were 10 -</p>		

Experiment report (continued):

30 % less than the controls. No differences are seen at higher Q . At these total lipid concentrations aggregated and/or bent long rods³ are present. Thus taxol may affect the structure at longer length scales associated with the organization and interaction of the rods. Unfortunately we could not follow this into the vesicle transition region and beyond due to loss of beam.

Conclusions: The presence of small amounts of taxol may affect the structure and association of rod-like mixed micelles. This could affect the formation of vesicles. However, more measurements will be needed in the vesicle transition and vesicle regions of the dilution series to determine this.

TAXOL
I

References:

1. Hjelm, R.P., Thiyagarajan, P., and Alkan, H. (1988), *J. Appl. Cryst.*, **21**, 858-863.
2. Hjelm, R.P., Thiyagarajan, P., and Alkan, H. (1990), *Mol. Cryst. Liq. Cryst.*, **180A**, 155-164.
3. Hjelm, R.P., Thiyagarajan, P., Sivia, D., Lindner, P., Alkan, H., and Schwahn, D. (1990), *Prog. Coll. Polymer Sci.*, **81**, 225-231.
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**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 LANSCE target's bulk biological shielding. 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 ($D\theta/\theta$) is $\pm 5\%$ for horizontal surfaces, and the horizontal resolution ($D\theta$) 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 PSR repetition rate, this chopper defines the wavelength band (1-16 Å or 16-32 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. Possible 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 incidence 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.

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 ^3He tube 1-mm resolution linear ^3He position-sensitive detector
Minimum reflectivity	10^{-6}
Typical run duration	30 min to 6 hr

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

Instrument used: <i>(please type)</i> SPEAR	Local contact: W.A. Hamilton	Proposal number: <i>(for LANSCE use only)</i> 3322.0
Title: A Neutron Reflectometry Study of the Mass Transport of Boron Atoms in Amorphous Elemental Boron		Report received: <i>(for LANSCE use only)</i> 3/1/91
Authors and affiliations: K. M. Hubbard, M. Nastasi, J-P. Hirvonen, T. Zocco & A.C. Lawson Materials Science & Technology Division, Los Alamos National Laboratory W.A. Hamilton & G.S. Smith LANSCE, Los Alamos National Laboratory		
Experiment report: <p>We have begun a series of neutron reflectivity experiments to study the mass transport of boron atoms in amorphous elemental boron. Our samples are nanometer scale $^{10}\text{B}/^{11}\text{B}$ bilayers and multilayers deposited by electron beam evaporation onto silicon substrates. The isotopically enriched boron layers have a high neutron contrast, so that the interference features of reflectivity profiles are extremely sensitive to changes in the compositional depth profile resulting from diffusion across interfaces. This technique is especially applicable to amorphous materials, for which diffusion lengths must be minimized in order to avoid unwanted crystallization.</p> <p>Initial reflectivity measurements were on samples consisting of five sequential bilayers, ($175 \text{ \AA } ^{11}\text{B}/275 \text{ \AA } ^{10}\text{B}$), for which a range of annealing temperatures (300°C, 400°C and 800°C) and times (as deposited, 30 m, 2 h, and 8 h) was surveyed. At 300°C, the diffusivity was too small to be conveniently measured with these samples - the reflectivity profile obtained for the 8 h sample was nearly identical to that of the as-deposited sample. At the other extreme of 800°C, the rapid disappearance of the Bragg peaks suggested that the interdiffusion of the multilayers was complete after only 30 m. This result was unexpected given the high melting point of boron (2030°C), which suggests a large activation energy for migration [1]. The data for the samples annealed at 400°C did exhibit a systematic decrease in the intensities of the interference maxima. Using the analysis technique described by DuMond and Youtz [2], the results for the 0-2 h anneals indicated a diffusivity ten times greater than that observed over the period of 2-8 h. Enhanced diffusivities in the initial stages of annealing have previously been observed in experiments on amorphous samples, and have been attributed to the initially enhanced defect concentration resulting from the presence of excess free volume [3]. As shown in Figure 1, the annealing out of the free volume from the boron samples in this experiment was reflected by a shift in the location of the interference maxima, which indicated a decrease in the film thickness of 3%. Variations in the thicknesses of the sequential bilayers prevented reliable fits to the data, complicating the extraction of accurate diffusivity values. Estimated values are on the order of $10^{-17} \text{ cm}^2/\text{s}$ in the interval of 0-2 h, and $10^{-18} \text{ cm}^2/\text{s}$ beyond, but it should be noted that the analysis technique described in Ref.2 breaks down for highly absorbing materials such as ^{10}B. A more detailed analysis of this data is underway.</p> <p>In order to alleviate the problems caused by thickness variations, measurements were also performed on bilayers ($430 \text{ \AA } ^{11}\text{B}/250 \text{ \AA } ^{10}\text{B}$). These samples were annealed at 400°C for times of 0 m (as-deposited), 15 m, 30 m, 68 m, 2 h, 4 h, 8 h, and 33 h. Selected reflectivity profiles are shown in Figure 2. Initially the reflectivity profiles are dominated by interference fringes due to the strongly scattering ^{11}B layer. For the samples annealed up to 68 m, interdiffusion at the single $^{10}\text{B}/^{11}\text{B}$ interface results in a gradual decrease in the visibility of these fringes. For longer anneals, the data developed the</p>		

Experiment report (continued):

character of a uniform mixture as boron began to penetrate to the two outer interfaces. After annealing for 8 h, the reflectivity profile was essentially equivalent to that of a homogeneous mix of the two isotopes in a layer 640 Å thick. Computerized fitting routines were used to analyze the reflectivity profiles for samples annealed up to 68 m. The results are consistent with a diffusivity on the order of 10^{-17} cm²/s, similar to that obtained for the multilayers. Additional analysis is underway for the data on longer anneals.

The multilayer and bilayer results both suggest that the as-deposited samples contain significant excess free volume. This provides a copious source of mobile defects, which significantly enhances the diffusivity during the initial stages of annealing. A major aim of future proposed work will be measurements on amorphous samples closer to the theoretical density. These will be prepared by ion-beam assisted deposition, and should provide a better measure of the intrinsic diffusivity of boron.

Figure 1: Reflectivity profiles for the multilayer samples annealed to various times at 400°C.

Figure 2: Reflectivity profiles for the bilayer samples annealed to various times at 400°C.

References:

- [1] A.M. Brown and M.F. Ashby, *Acta Metall.* **28**, 1085 (1980).
- [2] J. DuMond and J.P. Youtz, *J. Appl. Phys.* **11**, 357 (1940).
- [3] B. Cantor and R.W. Cahn, in *Amorphous Metallic Alloys*, edited by F.E. Luborsky, p.487.

Instrument used: (please type)	Local contact:	Proposal number: (for LANSCE use only)
Reflectometer	G. Smith, W. Hamilton	3339
Title: Chain End Segregation in Polystyrene Films		Report received: (for LANSCE use only)
3/12/91		
Authors and affiliations: Greg Beaucage, R.S. Stein, T. Mansfield (University of Massachusetts/Amherst) R. C. Composto (University of Pennsylvania) M. Satkowski, S. Smith (Procter and Gamble Corporation, Central Research Department, Cincinnati OH) W. Hamilton, G. Smith (Los Alamos National Laboratory)		
Experiment report: <p>The surface tension of polymers tends to increase with molecular weight¹. This behavior has been described by the equation^{2,3},</p> $\gamma = \gamma_{\infty} - \frac{k}{M_n^{2/3}} \quad (1)$ <p>γ_{∞} is the surface tension at infinite molecular weight and k is a constant which can be thought of as an end group contribution. Equation 1 is based on the assumption that chain ends segregate to the surface and serve to decrease the surface tension of low molecular weight polymers due to the presence of a relatively higher fraction of chain ends.</p> <p>It was the purpose of this experiment to determine the extent of end group segregation in polystyrene in an extreme case, that of the polystyrene/air and polystyrene/silicon surface. For this purpose block copolymers were synthesized with either deuterated end groups and hydrogenous main chains or hydrogenous end groups and deuterated main chains. Two homologous sets of copolymers were synthesized, one having a total molecular weight of 5 kg/mole and one set of about 65 kg/mole.</p> <p>Neutron reflection measurements were made on thin films spun from dilute toluene solutions of the block copolymers onto silicon wafers. Samples were dried under vacuum without heating (in such spinning solvent removal is not a serious problem.). Reflectivity measurements were made without annealing in order to</p>		

Experiment report (continued):

obtain a background profile for comparison with annealed films. (It was believed that the unannealed, spun films would show a reflectivity profile without segregation since solvent evaporation occurs very rapidly (less than one second) essentially locking in a fairly random distribution of the polymer chains.) The films were then annealed above the glass transition temperature for an extended period and a comparative profile was measured. In the annealed samples it was believed that segregation of the chain ends would be observable as a shift in the reflectivity pattern.

In all of the samples measured segregation of the chain ends was not observed (these results are in agreement with experiments done on similar polystyrene samples at Argonne National Lab by B. Sauer and D. Walsh⁴). Changes in thickness for the spun films were observed indicating that the materials had sufficiently annealed for stress relaxation via viscous flow to occur. These experiments served to disprove the widely used assumption that chain end segregation is responsible for changes in the surface tension with molecular weight. An alternative theory for surface tension changes has been developed based on the introduction of surface anomalies, such as chain folds, with increasing molecular weight (equation 2).

$$\gamma(T, M_n) = (T_c/T) \left(\gamma_0 + \gamma_\Delta \left(1 + \operatorname{Erf} \frac{M_n - M_{n \text{ lin}}}{M_{n \text{ range}}} \right) \right) \quad (2)$$

where γ_0 (= 25.43 dynes/cm for PS) is the surface tension for a low molecular weight material, γ_Δ (= 1.26 dynes/cm) is a measure of the effect of chain folds on surface tension, T_c (= 467.5 K) is a constant, $M_{n \text{ lin}}$ (= 2.21 kg/mole) is the molecular weight of a chain segment which can be accommodated on the surface and $M_{n \text{ range}}$ (= 2.73 kg/mole) is the width of the molecular weight range over which the chains go from no folds to a maximum number of folds. (Erf is the error function.) This theory can account for the molecular weight dependence of surface tension in polystyrene. Analysis of the neutron reflection data in terms of this theory are presently being conducted.

References:

- 1 S. Wu, Polymer Surface and Adhesion, Marcel Dekker, inc. NY, 1982 p. 72 and 169.
- 2 D. G. LeGrand and G. L. Gaines, Jr., J. Colloid Interface Sci., **31**, 162 (1969)
- 3 D. G. LeGrand and G. L. Gaines, Jr., J. Colloid Interface Sci., **42**, 181 (1973)
- 4 B. Sauer and D. Walsh, Personnel Communication 10/90.

Instrument used: <i>(please type)</i> SPEAR	Local contact: Dr. Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 3347
Title: CHARACTERIZATION OF NOVEL LANGMUIR-BLODGETT FILM STRUCTURES		Report received: <i>(for LANSCE use only)</i> 3/8/91
Authors and affiliations: Josef Michl and Thomas F. Magnera Center for Structure and Reactivity Department of Chemistry and Biochemistry University of Texas at Austin Austin, TX 78712-1167 After June 1, 1991: Department of Chemistry and Biochemistry University of Colorado Boulder, CO 80309-0215 Greg Smith, LANSCE		
Experiment report: <p>Over the last four years, we have been developing a set of rod-like straight and inert molecules ([n]staffanes) with terminal functionalities, suitable for a variety of uses. One of these has been the formation of monolayers. Unlike conventional monolayers built from flexible alkane chains, the monolayers built from stiff rods offer essentially no opportunity to the terminal groups to interfere chemically with each other and promise a variety of novel applications. Before their potential can be utilized, their structure has to be established. We have already obtained a fair amount of information using FT-IR, ellipsometry, and X-ray diffraction, and last year we started to use neutron diffraction to answer questions for which it is ideally suited. Promising preliminary results were obtained.</p> <p>Multilayer LB films of [n]staffane carboxylic acids (1) with the hydrocarbon end exposed at the surface are found, surprisingly, to become hydrophilic slowly with time as judged by the measurement of contact angles. Quartz microbalance experiments show that a large amount of water can be absorbed by these films over several hours. This happens apparently without a significant increase in film disorder as there is no detectable change in the hydrocarbon part of the FT-IR spectrum or in the Bragg spacings as determined by X-ray reflectivity. In particular, we are interested in determining where the absorbed water resides in the films.</p>		

Experiment report (continued):

The long neutron scattering length of deuterium makes comparative neutron reflectivity experiments on dry and D₂O-treated LB films of these molecules a unique means for determining where the sites for water storage are. Preliminary results are presented in Table 1. They provide a hint that the wetted films expand slightly, do not shift the critical angle, and that occluded D₂O leads to strong out-of-plane scattering. While intriguing, these results are far from definitive. The experiments were conducted when a water moderator was used at the LANSCE facility and the signal-to-noise was less than optimum, leading to long data collection times and limiting the number of experiments.

Table 1

molecule	layers		Bilayer spacing	X-ray
Cd ⁺² (⁻ OOC ₄ -H) ₂	7	dry	33.3 ± 1 Å	32.2 Å
		wet	33.9 ± 1	
Cd ⁺² (⁻ OOC ₃ Bu) ₂	7	dry	34.7 ± 1 Å	33.2 Å
		wet	35.0 ± 1	

References:

Instrument used: <i>(please type)</i> SPEAR	Local contact: G Smith	Proposal number: <i>(for LANSCE use only)</i> 3362
Title: Neutron Reflectance Investigation of Block Copolymers at Interfaces		Report received: <i>(for LANSCE use only)</i> 3.1/91
Authors and affiliations: <p>DETERMINATION OF END - ADSORBED POLYMER DENSITY PROFILES BY NEUTRON REFLECTOMETRY.</p> <p>J. B. Field¹, C. Toprakcioglu^{1,2}, R. C. Ball¹, H. Stanley³, L. Dai¹, W. Barford⁴, J. Penfold⁴, G. Smith⁵, and W. Hamilton⁵</p> <p>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, USA</p>		
Experiment report: <p>ABSTRACT.</p> <p>Neutron reflection techniques were employed to investigate the density profile of polystyrene / polyethylene oxide (PS / PEO) block copolymers adsorbed from d-toluene onto quartz. The geometry employed allowed the neutron beam to pass through the quartz substrate and be reflected from the quartz / d-toluene 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.</p>		

Experiment report (*continued*):

The above paper has been submitted to "Macromolecules".

References:

Instrument used: <i>(please type)</i> SPEAR	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 100023
Title: Characterization of Beta-Layers		Report received: <i>(for LANSCE use only)</i>
Authors and affiliations: J. K. Hoffer and R. J. Candler, P-10 M. Salazar and L. R. Foreman, MST-7		
Experiment report: <p>Introduction</p> <p>Beta-layering is a recently discovered 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 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.</p> <p>Experiments</p> <p>During the 1990 LANSCE run cycles, two attempts were made on the SPEAR apparatus to radiograph prototype ICF targets. In both cases, no ^3He accumulation was observed. However, in both cases, the target was <u>later</u> found to contain <u>no</u> DT. This proves that air does not decompose to form ^3He. On the positive side, it should be noted that a SPEAR radiograph of a test target containing a D_2 - 1% ^3He mixture did detect the presence of the ^3He. This shows that the loss of the liquid hydrogen moderator, while reducing the sensitivity of the radiography to ^3He, was not responsible for the null results.</p>		

Cryogenics

During each experiment, the aluminum-shell target was held at 17.7 K (2 K below the triple point of DT), for a three-week long period. The first radiographs were taken about two hours after the initial cool-down, to allow time for beta-layering to complete. Subsequent radiographs were taken at approx. one-week intervals. The entire refrigerator-cooled cryostat was removed from the beam tunnel during these inactive periods, but was kept running at all times to prevent melting of the DT. The cryostat had been designed with long electrical cables and an on-board vacuum system to accommodate these moves. The procedures developed prior to and refined during the actual experiments helped us carry out these awkward logistics flawlessly.

Tritium Handling

The SOP for handling the DT-filled aluminum targets was also refined during the course of the experiments. These procedures went very smoothly, thanks in large part to the attentive cooperation of HSE-11. No tritium contamination occurred. Even though the aluminum spheres later were shown to be empty, each time due to blockages of epoxy at the fill tube joints, the fill tubes themselves did contain approximately 1.1 Ci. Thus we can boast that we really did have tritium on site, and that our safety procedures were not in vain.

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 are sufficiently encouraged by our experiences to attempt the experiments again. We shall have to develop additional procedures to confirm that the targets are actually fully loaded.

References:

Instrument used: <i>(please type)</i> SPEAR	Local contact: W.A. Hamilton	Proposal number: <i>(for LANSCE use only)</i> 900901
Title: Neutron Reflectivity of Nickel Titanium Multilayers		Report received: <i>(for LANSCE use only)</i> 5/31/91
Authors and affiliations: E.M. Larson and A.F. Jankowski Chemistry and Materials Science Department Lawrence Livermore National Laboratory Livermore, CA 94550 W.A. Hamilton and G.S. Smith LANSCE		
Experiment report: <p>Very brief measurements (30 minutes each) were made of the neutron reflection characteristics of two Nickel Titanium multilayer structures fabricated at LLNL by sputter deposition on 50 mm diameter Si (111) substrates.</p> <p>3-90-0725 Nominal: 930 Å Ni / 950 Å Ti / 870 Å Ni/ Si 3-90-0314 Nominal: 32 Å Ni/ 77*(32 Å Ni/22 Å Ti) /Si</p> <p>The reflection profile for the Ni/Ti/Ni trilayer on Si, 3-90-0725, is shown in Figure A. These measurements covered the scattering vector range Q 0.01 to 0.12 Å⁻¹ with the instrument resolution varying from 3 to 4% FWHM over this range. For comparison the solid line is the calculated reflectivity profile (including instrument resolution) of the nominal layer structure assuming a 50 Å RMS roughness at the Ni/Ti interfaces and the free Ni surface. At the higher Q values in the calculated profile reflection from the Ni/Si interface dominates. The calculation assumes a 10 Å RMS roughness for this interface, characteristic of conventionally polished Si wafers, and the fit to the data is quite good in this region. Clearly at low Q the interference features of measured reflectivity are much less pronounced than for the calculated profile even for the relatively extreme roughness chosen.</p> <p>The repeat spacing for the 77 repeat bilayer structure, 3-90-0314, was initially characterized by x-ray diffraction. The neutron reflection profile measurement, figure B, covered the Q range from 0.015 to 0.2 Å⁻¹ with</p>		

Experiment report (continued):

the instrument resolution varying from 3 to 5% FWHM. While the Bragg reflection peak in the neutron reflection measurement at $0.116 \text{ \AA}^{-1}$, was consistent with the nominal $54 \text{ \AA}$ multilayer repeat distance confirmed by the x-ray measurements, reflection calculations failed to give any sort of reasonable fit to this data. As with the first sample the profiles observed would seem to be characteristic of a density profile distorted by extreme interfacial roughness or more probably the severe rippling observed in earlier samples [1,2].

References:

- [1] A.F. Jankowski & M.A.Wall, *Thin Solid Films* **181**, 305-312 (1989).
- [2] E.M. Larson, A.F. Jankowski, W.A. Hamilton & G.S. Smith, *Reflectivity Studies of Ni/Ti Neutron Mirrors*, LANSCE Experimental Reports 1989.

Instrument used: <i>(please type)</i> SPEAR	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 3333.0
Title: "Structure of the P-beta' phase of DMPC as a function of the number Langmuir-Blodgett Bilayers"		Report received: <i>(for LANSCE use only)</i> 2/28/91
Authors and affiliations: Gregory S. Smith, Los Alamos National Laboratory. William A. Hamilton, Los Alamos National Laboratory. Dipen Sinha, Los Alamos National Laboratory. Guy Danner, Los Alamos National Laboratory.		
Experiment report: <p>Phospholipids have been studied as model biomembranes since the bilayer model was first proposed by Danielli and Davson in 1935¹. The questions most often posed are "What is the structural arrangement of these molecules in the bilayers and what relation does this structure have with their functions in living systems." Starting with the pioneering work of Luzzati², x-ray scattering techniques were applied to this problem. The scattering studies, including more recent work^{3,4,5}, have shown that these molecules form a rich variety of lyotropic liquid crystalline phases as a function of concentration and temperature. However, several aspects of their structure in the biologically relevant liquid crystalline phases are not understood.</p> <p>These molecules are composed of two hydrocarbon chains, "the tails," connected to a glycerol "backbone" which is bonded to a zwitterionic "head group". When these molecules are mixed with water, they spontaneously form a repeated bilayer structure. Recently, we performed x-ray scattering experiments on freely suspended, hydrated films of dimyristoyl phosphatidylcholine (DMPC) to determine the in-plane structure of these molecules in the bilayer phases^{3,4,5}. In this work, we found that the previously identified L-beta phase consisted of three separate phases (Figure 1) distinguished by the orientation of the chains with respect to the in-plane lattice. Figure 2 shows the projection of the tails onto the bilayer plane for the three L-beta phases. Also, we found that the wave-vector of the macroscopic ripples (100-200Å) of the Pβ' phase was tilted with respect to the bilayer normal with an angle of 7.5 degrees⁵. The transitions between these phases conform to recent theories⁶ suggesting that these are a special type of continuous hexatic phase transition. Since the freely suspended film technique does not allow for accurate control of the number of bilayers, n, within a film, it is difficult to study single oriented domains or structure as a function of n.</p> <p>We have attempted to prepare single crystalline domains of these materials using the Langmuir-Blodgett technique. This involved floating a monolayer of DMPC on the water in the Langmuir trough. Then a silicon substrate was passed through the water-air interface and the first layer was transferred to the substrate. However, unlike other materials, we were unable to transfer more than a monolayer. In fact, attempts at a second monolayer deposition pulled part of the first</p>		

Experiment report (continued):

monolayer from the silicon. In light of this, we attempted to create thicker samples by dissolving the lipids in chloroform (25mg/ml) and spinning the solution onto a polished silicon wafer.

The results of the scattering from two such samples are shown below. In each case, the lipid was deuterated and the samples were placed in a humid atmosphere of D₂O during the reflection measurements. Figure 1, is the reflection profile of a sample made by spinning the silicon at approximately 10 RPS and adding 1ml of solution to the wafer. The solid curve is the calculated reflectivity expected from one and a half bilayers on the silicon. Although the form of the calculation is close to the data, the fit is not very good. Worse yet, we see that for sample #2 which had 3ml of solution added, there is a single peak corresponding to that of the one and a half bilayers yet is much sharper. If we were adding layers with the addition of more solution we would have expected more peaks. This all suggests that the films were inhomogeneous and therefore were not appropriate for these experiments. We are continuing to investigate methods of sample preparation for these measurements.

Figure 1

Figure 2

References:

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- (2) V. Luzzati, *Biol. Membr.*, **1**, 71(1968); A. Tardieu, V. Luzzati, and F. Reman, *J. Mol. Biol.*, **75**, 711(1973).
- (3) G. S. Smith, C. R. Safinya, D. Roux, and N.A. Clark, *Mol. Cryst. Liq. Cryst.*, **144**, 235(1987).
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Instrument used: <i>(please type)</i> SPEAR	Local contact: Greg Smith	Proposal number: <i>(for LANSCE use only)</i> 900904
Title: Diffuse Scattering from Rough Thin Films		Report received: <i>(for LANSCE use only)</i> 6/27/91
Authors and affiliations: W. A. Hamilton, R. Pynn, and G. Smith LANSCE		
Experiment report: <p>The intent of this experiment was to mimic with neutrons an experiment first carried out by Newton [1] with light. Newton observed interference fringes when he allowed light to be reflected by a dusty, silvered mirror. These fringes are due to interference between two light rays scattered by each dust particle. One ray is reflected from the silvered surface and is then scattered by the dust particle, while the other is first scattered by the dust particle and then reflected by the silvered back of the mirror.</p> <p>In attempt to imitate this experiment with neutrons, we used two systems: (a) a 400 Å titanium film deposited on sapphire and (b) and 500 Å gold film deposited on a silicon wafer, with 50 Å diameter gold "balls" spread on top of the film (colloidal gold particles — the gold "balls" — suspended in a toluene carrier were kindly supplied by Jess Wilcoxon of Sandia Laboratory). While diffuse fringes were observed with both samples, the titanium film gave the best data. Figure 1 is a grey-scale plot of scattered neutron intensity as a function of neutron wavelength (abscissa) and grazing angle α of reflection (ordinate) for the Ti/sapphire sample. The bright modulated stripe running from right to left is the specular scattering, while the inclined fringes are diffuse scattering. It should be noted that, except at small wavelengths, the wavelength bins used in the figures have widths that are proportional to the value of the wavelength at the centre of the bin. The incident neutron spectrum has not been divided out of the data shown in the figures.</p> <p>A theoretical description of the observed diffuse scattering has been attempted in terms of a generalised Born approximation. Within this theory it is possible to calculate the diffuse scattering by a thin film with one or two rough interfaces. Figures 2,3, and 4 show results obtained for a 400 Å titanium film on a sapphire substrate in three situations: figure 2 — a smooth titanium/sapphire interface and a titanium/air interface with a self-affine Gaussian roughness of standard deviation 20 Å; figure 3 — uncorrelated 20 Å roughness at both surfaces of the titanium film; figure 4 — perfectly correlated roughness at the two film surfaces. Comparison of the theoretical and experimental results indicates that there is considerable correlation between the roughnesses of the two surfaces of the titanium film. It thus appears that diffuse neutron scattering can be used to probe the degree of conformality of the two rough surfaces of a film.</p>		

Experiment report (continued):

Figure 1:

Figure 2:

Figure 3:

Figure 4:

References:

Sir Isaac Newton, *Opticks* (originally published in London, 1704; new edition by Dover Publications Inc., New York, 1952), p 289 ff.

Instrument used: (please type) SPEAR	Local contact: W.A. Hamilton	Proposal number: <i>(for LANSCE use only)</i> 900906
Title: Specular Reflection from a Directionally Polished Glass Surface		Report received: <i>(for LANSCE use only)</i> 5/31/91
Authors and affiliations: W.A. Hamilton, G.S. Smith & R. Pynn LANSCE		
Experiment report: <p>The effects of surface and interfacial roughness on neutron reflection measurements have usually been modelled using the Debye-Waller style modification of the sharp interface reflection coefficient $R_0(k_{\perp})$ developed by Névot and Croce [1] in the context of X-ray reflection:</p> $R(k_{\perp}) \approx \exp\{-4\sigma^2 k_{\perp} k'_{\perp}\} R_0(k_{\perp})$ <p>Here $k_{\perp}$ and $k'_{\perp}$ are the wavevector components perpendicular to the surface of the incident and refracted beams. The surface is characterized by the single parameter σ; the standard deviation of the surface height distribution $\langle z[[\mathbf{r}]z[\mathbf{r}]]_{\mathbf{r}}$. Recent work by Sinha et al. [2] and Pynn [3] treats neutron and X-ray scattering in reflection geometry more rigorously, obtaining expressions for off-specular scattering in terms of the full height-height autocorrelation of the surface $\langle z[[\mathbf{r}+\mathbf{R}]z[\mathbf{r}]]_{\mathbf{r}}$. Sinha et al. made specular and diffuse X-ray scattering measurements for the demonstration case of a polished Pyrex glass surface and obtained good agreement with their formalism.</p> <p>The present work represents the application of this work to a case in which the height-height autocorrelation of the surface is anisotropic in the plane. Neutron reflection and diffuse scattering measurements were made for a standard piece of neutron guide glass [4] which had been preferentially polished in one direction, rather than with the usual circular motions. We therefore expect a surface morphology similar to that shown in the drawing, resulting in a surface more correlated along the direction polishing "furrows" than at an angle to them.</p> <p>Measurements were made at a variety of angles between the specular reflection scattering plane and the polishing direction. The preliminary data shown represent "near-specular reflection coefficients",</p>		

Experiment report (continued):

determined in the usual way from the sum of measurements within the collimation of the incident beam, for neutrons incident along the polishing furrows ($\phi=0^\circ$) and across them ($\phi=90^\circ$). As we would expect, the apparent roughness of the surface is strongly dependent on sample orientation. Applying the Névot and Croce expression to these reflection profiles we would obtain values for the RMS "roughness" of this surface of 22 Å and 35 Å respectively.

While the present case is certainly trivial, it represents a reasonably well controlled example of a situation which could easily arise in more interesting situations and lead to serious interpretation problems. Some thin film production methods, for example spin casting, involve stresses we might expect to result in similar surface morphologies.

Analysis is continuing on the diffuse scattering measurements.

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- [1] L. Névot and P. Croce, *Caractérisation des surfaces par réflexion rasante de rayons X*, Revue Phys. Appl. **15**, 761 (1980).
- [2] S.K. Sinha, S.B. Sirota, S. Garoff and H.B. Stanley, *X-ray and neutron scattering from rough surfaces*, Phys.Rev. B **38**, 2297 (1988).
- [3] R. Pynn, to be published.
- [4] Cilas-Alcatel Borkron glass.

Instrument used: <i>(please type)</i> <p style="text-align: center;">SPEAR</p>	Local contact: <p style="text-align: center;">HAMILTON / SMITH</p>	Proposal number: <i>(for LANSCE use only)</i> <p style="text-align: center;">3329</p>
T <p style="text-align: center;">THE MOLECULAR WEIGHT DEPENDENCE OF THE INTERFACE BETWEEN HOMOPOLYMERS</p>		Report received: <i>(for LANSCE use only)</i> <p style="text-align: center;">3/1/91</p>
Authors and affiliations: <p style="text-align: center;">T. P. Russell IBM Almaden Research Center, San Jose, California 95120</p> <p style="text-align: center;">W. A. Hamilton, G. S. Smith Los Alamos National Laboratory, Los Alamos, NM 87545</p>		
REPORT <p>The interface formed between polystyrene, PS, and poly(methylmethacrylate), PMMA, homopolymers was investigated as a function of the concentration of the molecular weights of the homopolymers. A matrix of experiments were performed on bilayers of PS and perdeuterated PMMA where the molecular weight of both components were varied from 10^4 to 5×10^5. Specimens were prepared by casting a film of the d-PMMA onto a Si substrate. The thickness of the d-PMMA layer was $\sim 10^3 \text{ \AA}$. Onto a separate substrate a film of PS was prepared and the film was floated off onto a pool of water. This film was retrieved using the coated Si substrate forming a bilayer specimen. The bilayer was annealed at 150°C for 240 hrs under vacuum to allow the homopolymers to come to equilibrium and were then quenched to freeze in the structure at the higher temperatures. It should be mentioned that the transfer of films where the molecular weights of the homopolymers are $\sim 10^4$ is rather difficult since the films are brittle. However, confinement of the film on the water surface using barriers prevented the film from fragmenting significantly. Cracks on the surfaces of these films were observed but their presence did not perturb the reflectivity measurements. This is due to the fact that the fraction of the surface that was occupied by the cracks was small in comparison to the total area of the interface between the homopolymers.</p> <p>A typical reflectivity profile for the bilayer specimens is shown in Figure 1. As expected the reflectivity profile exhibits a pronounced fall off above the critical angle with a damped, single frequency oscillation. The scattering length profile of the bilayered film is such that the reflectance at the air/PS interface plays a minor role, whereas the reflectances at the PS/d-PMMA and the d-PMMA/Si interfaces dominate. To a first approximation the reflectivity profile is essentially the reflectivity profile of a single d-PMMA layer on an Si substrate. Knowing the thickness of the individual layers from optical ellipsometry reduces the number of parameters in these experiments to only the width of the interface between the PS and d-PMMA layers. The scattering length density profile shown in the inset was used to calculate the reflectivity profile shown as the solid line in the figure.</p>		

We define the interfacial width, a_i , as the slope of the gradient at the midpoint in the concentration profile. Shown in Figures 2 and 3 are the interfacial width as a function of the molecular weight of the PS and of the d-PMMA, respectively. As can be seen, the interfacial width at high molecular weights is equal to 50 Å in agreement with previous studies.^{1,2,3} However, as the molecular weights of the homopolymers decrease the interfacial width increases. This would be expected from the reduction in the interfacial tension with a decrease in the molecular weight. However, the limited molecular weight range precludes assessment of an accurate power law dependence.

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2. Fernandez, M.L., Higgins, J.S., Penfold, J., Ward, R.C., Shackleton, C., Walsh, D.J. 1988. *Polymer* 29:1923-28
3. Anastasiadis, S.I.L., Russell, T.P., Satija, S.K., Majkrzak, C.F. 1989. *J. Chem. Phys.* 92:5677-91

Instrument used: (please type) SPEAR	Local contact: HAMILTON / SMITH	Proposal number: (for LANSCE use only) 3329.1
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**THE WIDTH OF HOMOPOLYMER INTERFACES IN THE
THE PRESENCE OF SYMMETRIC DIBLOCK COPOLYMERS**

Report received:
(for LANSCE use only)

5/1/91

T. P. Russell, A. Menelle
IBM Almaden Research Center, San Jose, California 95120

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REPORT

The interface formed between polystyrene, PS, and poly(methylmethacrylate), PMMA, homopolymers was investigated as a function of the concentration of added symmetric diblock copolymers of PS and PMMA, denoted P(S-b-MMA), using neutron reflectivity. Specimens were prepared by casting films of perdeuterated PMMA onto a Si substrate having a thickness of $\sim 10^3 \text{\AA}$. Onto a separate substrate a film of P(S-b-MMA) was prepared where the thickness of the film was varied from $\sim 75 \text{\AA}$ up to $\sim 350 \text{\AA}$ by variation of the concentration of the casting solution. The PMMA block of the copolymer was perdeuterated. This film was floated off onto a pool of water and retrieved with the d-PMMA coated substrate. A film of PS, $\sim 10^3 \text{\AA}$, was then prepared on a separate substrate, floated off onto a pool of water and retrieved with the coated substrate forming, thereby, a trilayered specimen. The trilayer was then heated to 160°C for 120 hrs. to allow the homopolymer and block copolymer molecules to come to equilibrium. The specimens were then quenched to room temperature, freezing in the structure at the higher temperatures.

A typical reflectivity profile from specimens where the initial thickness of the P(S-b-MMA) layer was less than $\sim 250 \text{\AA}$ is shown in Figure 1. The reflectivity profile exhibits the usual critical angle followed by a reduction in the reflectivity as one proceeds to high neutron momenta. A single frequency oscillation is superposed on the reflectivity profile. The interpretation of these reflectivity profiles is rather trivial. Given the labelling of the homopolymers and copolymers it is not possible to distinguish between the PS or PMMA segments of the copolymer or homopolymers and, consequently, the trilayered specimen reduces to a simple bilayer specimen with an interface separating the PS and d-PMMA layers. It is, in fact, this interfacial width that is of importance to this particular study. Measurements of the sample thickness by optical ellipsometry served to eliminate the specimen thickness as parameters in the profile analysis. Thus, the only true variable in the problem was the interfacial width. In all cases either a hyperbolic tangent function or an error function could describe the variation in the concentration of components across the interface. We shall define the interfacial as the slope of the interface profile at the mid-point in the composition variation.

Shown in Figure 2 is the interfacial width, a_1 , as a function of the thickness (or concentration) of the copolymer layer placed at the interface. In the absence of the diblock copolymer a_1 is 50Å which agrees with previous measurements^{1,2,3}. As the amount of copolymer is increased, however, a_1 gradually increases up to ~80Å when the thickness of the copolymer layer is ~250Å. This thickness corresponds to one-half the thickness of the lamellar microdomain morphology in the bulk which translates into effectively a mono-molecular layer of the copolymer at the interface between the homopolymers. This interfacial broadening represents an interpenetration of the homopolymer and diblock copolymer segments at the interface even though the molecular weights of the components would dictate that there should be minimal penetration of the homopolymer into the interfacial region.

Further addition of copolymer to the interface results in a pronounced broadening of the interfacial width. In fact, the amount of off-specular scattering observed in these experiments increased dramatically as well. This indicates that there is either micelle formation at the interface or the interface exhibits a marked curvature. The distinction between these two possibilities is currently being pursued. However, the major point to be learned from these results is that excess copolymer at the interface results in a major perturbation of the structure of the interface.

It has, also, been shown previously that the interface between the lamellar microdomains in a multilayered morphology is 50Å.^{1,3} Thus an interfacial broadening must be observed in this morphology as homopolymer is added to the diblock copolymer to be consistent with the above results. Experiments were performed on mixtures of PS, PMMA and P(S-b-MMA) where equal amounts of the homopolymer were added to the copolymer and where either all the PS or PMMA segments (homopolymer or copolymer) had the same labelling with deuterium. A typical reflectivity profile for a 10% d-PS, 10% PMMA and 80% P(d-S-b-MMA) mixture is shown in Figure 3. Analysis of the reflectivity profiles from these mixtures is again straightforward since the mixtures, up to ~20% homopolymer addition, form a multilayer structure. This is evidenced by the appearance of the distinct Bragg reflections in the reflectivity profiles. The scattering length density profile shown in the inset was used to calculate the reflectivity profile shown as the solid line in the figure. The concentration profile across the interface was described by a hyperbolic tangent function. As expected the period of the multilayer increased with the addition of the homopolymer. More importantly, as shown in Figure 4, the interfacial width of the multilayer morphology was found to gradually increase with the addition of the homopolymer. Again, these results demonstrate that the homopolymer penetrates deeply into the interfacial region.

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2. Fernandez, M.L., Higgins, J.S., Penfold, J., Ward, R.C., Shackleton, C., Walsh, D.I. 1988. *Polymer* 29:1923-28
3. Anastasiadis, S.H., Russell, T.P., Satija, S.K., Majkrzak, C.F. 1989. *J. Chem. Phys.* 92:5677-91

Experiment report (continued):

References:

Instrument used: <i>(please type)</i> SPEAR	Local contact: G. Smith	Proposal number: <i>(for LANSCE use only)</i> 900903.0
Title: Reflectivity Measurements of the Pd(111)-Al ₂ O ₃ (0001) Interface		Report received: <i>(for LANSCE use only)</i> 3/1/91
Authors and affiliations: M.R. Fitzsimmons Sektion Physik Uni Muenchen Muenchen, West Germany		
Experiment report: <p>The purpose of this experiment is to determine whether the difference between the thermal expansion coefficients of Pd and sapphire alters the interfacial structure between single crystals of these materials at reduced and elevated temperatures. Specimens for this experiment had been earlier characterized with X-ray reflectivity and grazing incidence diffraction techniques at room temperature. The X-ray reflectivity profiles exhibited oscillatory behavior with scattering vector magnitude, which is expected from 50nm thick Pd overlayers on sapphire. Surprisingly, the neutron reflectivity profiles of the same specimens were found to be featureless even though Pd and sapphire exhibit significant neutron contrast. The inconsistency between the neutron and X-ray results is not yet understood.</p>

**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 1.5 - 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	37 - 620 meV (300 - 5,000 cm ⁻¹)*
Q range	1.5 - 17 Å ⁻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 ³ He (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*

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>										
FDS	Juergen Eckert	3323										
Title: Molecular Hydrogen Complexes of Rhenium and Iridium		Report received: <i>(for LANSCE use only)</i> 3 / 4 / 71										
Authors and affiliations:												
<table border="0"> <tr> <td>Craig M. Jensen</td> <td>University of Hawaii</td> </tr> <tr> <td>Mario Mediat</td> <td>University of Hawaii</td> </tr> <tr> <td>Andrew Wojcicki</td> <td>Ohio State University</td> </tr> <tr> <td>Juergen Eckert</td> <td>LANSCE, LANL</td> </tr> <tr> <td>G. J. Kubas</td> <td>INC-4, LANL</td> </tr> </table>			Craig M. Jensen	University of Hawaii	Mario Mediat	University of Hawaii	Andrew Wojcicki	Ohio State University	Juergen Eckert	LANSCE, LANL	G. J. Kubas	INC-4, LANL
Craig M. Jensen	University of Hawaii											
Mario Mediat	University of Hawaii											
Andrew Wojcicki	Ohio State University											
Juergen Eckert	LANSCE, LANL											
G. J. Kubas	INC-4, LANL											
Experiment report:												
<p>Vibrational spectra were obtained for both of these new molecular hydrogen complexes of this proposal, i.e. $\text{IrH}_2(\eta^2\text{-H}_2)\text{Cl}[(\text{P-}i\text{-Pr}_3)_2]$ and $[\text{ReH}_4(\eta^2\text{-H}_2)(\text{Cytpt})]\text{SbF}_6$, in both normal form and with the hydride and dihydrogen ligands replaced by deuterated ones. This experiment suffered from source reliability problems, as more than 16 days were required to complete the work. In addition, a loose connector on the Isolated Latch Module caused intermittent mixing of Be and BeO spectra in the first two runs of the Ir-complex, which had to be repeated. Nonetheless, with the use of discretionary time good data could be obtained.</p> <p><u>Ir-complex.</u> The sample with deuterated hydride and dihydrogen ligands was evidently not completely exchanged. Subtraction of its spectrum from that of the fully protonated form yielded a large negative peak at approximately 195 cm^{-1}. Since it is not possible that such an intense peak be associated with the dideuterium ligand, alternative explanations had to be sought. If the exchange did not go to completion, both HD and H_2 ligands would also be present in the "deuterated" sample. However, it was not possible to account for the data with the assumption that the 195 cm^{-1} peak was a transition of the HD ligand. Support for the idea that this peak is the torsional transition of the dihydrogen ligand came by way of the re-run of the protonated sample. Since it is known [1] that this sample can loose H_2 when not kept under 1 atm. of H_2 pressure, we can assume that in the rerun the sample had somewhat less dihydrogen complex. The difference spectrum (1st run - 2nd run; Fig. 1) does indeed show positive peaks at appr. 195 and 270 cm^{-1}. These can readily be identified [2] as the split excited librational state for a two-fold potential with a barrier height of about 1.1 kcal/m. Negative peaks are discernible at about 125 and 240 cm^{-1}. These can then be taken as the $J=0-1$ and $J=1-2$ transitions of the free H_2 that was lost from the complex. Additional bands at 390, 570, 810 and</p>												

Experiment report (continued):

930 cm^{-1} can then be tentatively assigned to the remaining two Ir-(H₂) deformation modes, the Ir-H bend, and the Ir-(H₂) stretch, respectively. Experiments are planned for the the ILL to measure the rotational ground state splitting as well. This is an essential additional piece of information for deciding the actual symmetry of the hindering potential.

IrH₅(H₂) complex

Fig. 1

Re complex [ReH₄(H₂)-(D₂)₂ (1.0 Å)]

Fig. 2

Re-complex. The difference spectrum [ReH₄(H₂)-ReD₄(D₂)][(Cytpp)]SbF₆ is shown in Fig. 2. Because of the large number of hydride ligands and possible interactions between them the vibrational data are not readily interpreted. Based on the known [3] strong Re-(H₂) binding we expect the torsion at fairly high frequencies. The peak at 360 cm^{-1} would appear to be the most likely candidate. If one uses the X-ray diffraction H-H distance (1.08 Å), B is now 28 cm^{-1} . For the two-fold potential this implies a tunnel splitting of 0.54 μeV . This would be extremely difficult to observe, and, in fact, experiments carried out by us on IN5 and IN10 at the ILL failed to observe rotational tunneling. While the latter results is somewhat unsatisfactory, it nonetheless agrees with the present observations.

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2. J. Eckert, G. J. Kubas, J. H. Hall, P. J. Hay and C. M. Boyle, *J. Am. Chem. Soc.* **112**, 2324 (1990).
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Instrument used: <i>(please type)</i> FDS	Local contact: Dr. Juergen Eckert	Proposal number: <i>(for LANSCE use only)</i> 3375
Title: INELASTIC NEUTRON SCATTERING BY MOLECULES IN MATRIX ISOLATION AND BY PARTIALLY ALIGNED MOLECULES		Report received: <i>(for LANSCE use only)</i> 3/8/91
Authors and affiliations: Josef Michl and J. George Radziszewski Center for Structure and Reactivity Department of Chemistry and Biochemistry University of Texas at Austin Austin, TX 78712-1167 After June 1, 1991: Department of Chemistry and Biochemistry University of Colorado Boulder, CO 80309-0215 Juergen Eckert, LANSCE		
Experiment report: <p>We have been successful in carrying out some initial experiments on partially aligned molecules under this program. Construction of the apparatus for the study of matrix isolated molecules was delayed because of manpower and budgetary difficulties. Funds had been set aside for purchase of commercially available perdeuterated polyethylene, and a small quantity was acquired for testing. It proved to be very difficult to stretch since it was high density material. We will now attempt to apply for funds to obtain low density polyethylene for this work as a custom synthesis, for which we have been quoted upwards of \$15K for a sufficient quantity.</p> <p>Because of these difficulties we took a preliminary step by collecting data on normal stretched polyethylene with approximately 1% of 1,2-dimethylnaphthalene dissolved in it. The sample was in the form of a stack of horizontal, aligned disks. The stretching direction was marked and put parallel to Q, and subsequently perpendicular. After collecting the spectra (all at low temperature) of the polyethylene in both orientations, the 1,2-dimethylnaphthalene was dissolved in it, and the experiment repeated.</p> <p>Despite the huge amount of scattering from the polyethylene itself, subtraction of the two spectra (with and without the 1,2-dimethylnaphthalene) not only yielded discernible features, but also showed differences in the two orientations (Fig. 1). All the peaks remaining after subtraction of the polyethylene itself can be attributed to 1,2-DMN, for which we do know the</p>		

Experiment report (continued):

Raman and IR spectra. They lie at appr. 240, 300, 490, 705, 860, 1430 and 1660 cm^{-1} in the spectrum for Q perpendicular to the stretching direction, and appr. 200, 300, 590, and 800 cm^{-1} for Q parallel. Assignments of these spectra are not very well known, and we intend to perform NCA calculations for this purpose, and to make optimal use of the information provided by the present IINS data.

Despite the rather disadvantageous signal-to-background ratio of this test experiment we have clearly demonstrated the promise of this technique. Further test experiments with more favorable geometries and some effort to reduce the large amount of multiple scattering in the original experiment would be well worthwhile until such time that the funds can be procured to obtain the perdeuterated low density polyethylene.

1,2-DMN/Poly - Poly Q perp.

1,2-DMN/Poly - Poly Q par.

References:

Instrument used: (please type) FDS	Local contact: J. Eckert	Proposal number: (for LANSCE use only) 3399.0
Hydrogen Bond Dynamics in Quinolinic Acid		Report received: (for LANSCE use only) 11/30/91

Authors and affiliations:

Horst Küppers, Mineralogisches Institut, Universität Kiel, FRG

Juergen Eckert, LANSCE

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 quinolinic acid (QNA; 2,3-pyridinedicarboxylic acid; $\text{C}_7\text{H}_3\text{H}_2\text{NO}_4$) on forms with the H-bond protonated and deuterated. There are two hydrogen bonds in the system¹, a weak $\text{N-H}\cdots\text{O}$ *intermolecular* H-bond, and a very strong $\text{O}\cdots\text{H}\cdots\text{O}$ *intramolecular* H-bond (Fig. 1). The latter is slightly asymmetric with OD distances of 1.15 and 2.25 $\text{\AA}$. Since the orientation of the molecules in the crystal (space group $\text{P2}_1/\text{c}$) is such that the H-bonds point in the same direction we had planned to carry out the experiments with oriented single crystals. Crystal growth, however, was unexpectedly slow and difficult. The results presented below were therefore obtained with polycrystalline specimens.

Figure 1

The spectra obtained at a temperature of approximately 12 K on the FDS are shown in the Maximum Entropy Reconstruction in Fig. 2. Pronounced differences between D-QNA and H-QNA can easily be discerned, and can be highlighted by direct subtraction of the spectra from each other. Since there are two rather different types of H-bonds in the material, we expect two sets of associated frequencies.

In accordance with some of our previous studies^{2,3} we can readily make the following tentative assignments. For the intramolecular OHO-bond the out-of-plane bend $\gamma(\text{OH})$ may be identified in the difference spectrum at about 1070 cm^{-1} while a broad band at about 1590 cm^{-1} (which is absent in D-QNA) is assigned to the in-plane-bend $\delta(\text{OH})$. The asymmetric stretch $\nu(\text{OH})$ for such a short H-bond is at very low frequencies, here at 600 cm^{-1} . The *intermolecular* NHO bond is much weaker. We find evidence for $\nu(\text{NH})$ at about 2960 cm^{-1} , and assign accordingly⁴ the shoulders at 920 and 1300 cm^{-1} to (respectively) $\gamma(\text{NH})$ and $\delta(\text{NH})$.

The above assignments must be considered as tentative. Single

Fig. 2. INS spectra of D-QNA and H-QNA

crystal data would be extremely important in confirming these assignments and in obtaining a better picture of the potential in three dimensions for this extremely short H-bond.

The remainder of the beam time allocation was utilized to complete work under previous proposals on the systems Li-H-Succinate and Li-H-Phthalate.

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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: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
FDS	Juergen Eckert	3419
Title:		Report received: <i>(for LANSCE use only)</i>
Temperature dependence of the vibrational spectra of of Acetanilide and its isotopomers		2/1/91
Authors and affiliations:		
Mariette Barthes, Universite Montpellier II, France Juergen Eckert, LANSCE, LANL Susanna Johnson, LANSCE, LANL Basil Swanson, INC-4, LANL		
Experiment report:		
<p>We have obtained the detailed temperature dependence of the vibrational spectrum of acetanilide (ACN), as well as rather limited temperature variation of the isotopomers ACN-d₅ (phenyl deuterated), ACN-d₃ (methyl deuterated) and ACN-d₆ (phenyl and H-bond deuterated). In addition, we measured the low temperature spectra of fully deuterated ACN, ACN-d₈ (phenyl and methyl deuterated) and the new compound ACN-F₃ (methyl fluorinated). Unfortunately, the spectra for ACN-d₈ were heavily contaminated with peaks from frozen water. The sample had evidently not been dried sufficiently after D/H exchange on the hydrogen bond. Nonetheless, the data obtained provide a number of new insights into the types of inter- and intramolecular vibrational coupling that is present in this material, and that may play a role in the energy transport mechanism of this biological model system.</p> <p>Shown in Fig. 1 is the region of the methyl torsion for three isotopomers at low temperature. It is immediately apparent that the structure in the methyl peak strongly depends on both the deuteration of the phenyl ring and the deuteration of the H-bond: vibrational coupling between modes associated with these molecular groups and the methyl group is thereby indicated. It should also be added, that the methyl torsion shows a very strong temperature dependence in the optical data ^{1,2} and in the single crystal Raman spectrum shows a pronounced temperature dependent splitting into three components which at present is unexplained.</p>

Experiment report (continued):

The coupling involving the H-bond proton is further amplified by our observation that the intrinsic width of $\gamma(\text{OH})$, the out-of-plane bending mode of the H-bond at about 750 cm^{-1} depends on the isotopomer: it is appr. 13 cm^{-1} for ACN, 15 cm^{-1} for ACN- d_3 and 18.3 cm^{-1} for ACN- d_5 . This type of coupling does indeed have a strong effect in the way the spectra broaden with temperature. Shown in the figure below are the data in the region of $\gamma(\text{OH})$ for ACN (left), ACN- d_5 (center) and ACN- d_3 (right) at three (or only two for ACN- d_3) temperatures. The rapid broadening of the $\gamma(\text{OH})$ peak for ACN is in marked contrast to that for ACN- d_5 , while we do not have enough data for ACN- d_3 to make such a comparison. A previous theory on the broadening of this peak in optical data invoked coupling with acoustic phonons [3], which no longer appears to be the only possible mechanism. From our data it has become clear that this line of investigation is extremely useful, and that we urgently require more time to do similar studies on the isotopomers ACN- d_8 and ACN- F_3 , as well as complete the temperature dependence for some of the isotopomers studied here.

References:

1. C. T. Johnston, S. F. Agnew, J. Eckert, B. I. Swanson and C. J. Unkefer, J. Phys. Chem. (in press)
2. M. Barthes et al., in **Nonlinear Coherent Structures**, Springer Lecture Notes in Physics 353, 1989.
3. G. Zerbi and G. Dellaplane, J. Raman Spec. **12**, 165 (1982).

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
FDS	Juergen Eckert	100019.0
Title: Vibrational Properties of PuH _x and PuD _x		Report received: <i>(for LANSCE use only)</i> 2/1/91
Authors and affiliations: Joyce A. Goldstone, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 Andrew C. Lawson, MST-5, Los Alamos National Laboratory, Los Alamos, NM 87545 Juergen Eckert, LANSCE, Los Alamos National Laboratory, Los Alamos, NM 87545 Lisa Diebolt, Arizona State University, Tempe, AR 85287 Barbara Cort, NMT-5, Los Alamos National Laboratory, Los Alamos, NM 87545 John W. Ward NMT-5, Los Alamos National Laboratory, Los Alamos, NM 87545 John M. Haschke NMT-5, Los Alamos National Laboratory, Los Alamos, NM 87545		
Experiment report: <p>The crystal structure, phase diagrams, and chemistry of the plutonium hydrides are similar to those of the later rare-earths hydrides. [1] In the CaF₂-type fcc structure assumed by these hydrides, first the tetrahedral sites (T-sites; 2 per metal), then the octahedral sites (O-sites; 1 per metal), are occupied. Incoherent inelastic neutron scattering offers a quick method to obtain information on the relative T- and O-site occupancies as well as on the lowering of the O-site symmetry. [2] Since the major influence on the frequency of the local H or D vibrational mode is the metal-hydrogen distance, the large difference in separation for a O-site H or D (approx. 2.67 Å) versus a T-site H or D (approx. 2.31 Å) usually permits a clean distinction to be made in the inelastic spectrum as to the H or D site contributing to a given vibrational peak. In this experiment, we collected data on four samples, PuD_{2.33}, PuD_{2.70}, PuH_{2.33}, and PuH_{2.70} at 10 K. In all these samples, both octahedral and tetrahedral sites are occupied.</p> <p>The three figures on the next page give examples of the data collected on these samples. The upper two figures give a comparison of the PuH_{2.33} and PuH_{2.70} vibrational spectra collected at 10 K. The same basic five features appear in both spectra. The lowest energy peaks at 600 cm⁻¹ (8 cm⁻¹ = 1 meV) and below are represent the vibration modes from the O-site hydrogen atoms. The energies of these peaks are approximately 68 and 75 meV, in reasonable agreement with the O-site energy range of other CaF₂-like structure hydrides. For perfectly cubic site symmetry of the O-site hydrogen, only one vibrational peak is expected. The presence of two peaks for the O-site hydrogen indicates either a lower site symmetry (possibly tetrahedral symmetry) or strong hydrogen-hydrogen interactions so that the vibration is not truly a local mode. The remaining three peaks (at roughly 800 and above cm⁻¹) in these two spectra are more likely identified with tetrahedral site vibrational modes. The appearance of three strong peaks in this energy regime has been observed in both NpD_{2.65}[3] and NdH_{2.62}[4] and has been tentatively associated with the fcc-hcp transition. The PuH_{2.7} sample is particularly near this transition concentration. The lower figure shows the PuD_{2.33} spectra taken at 10 K. The PuD_{2.7} sample gave a similar picture. The change in mass shifts the energy spectrum by $\sqrt{2}$. The energies of the five peaks observed in the hydrogen spectra should be shifted to approximately 380, 425, 588, 680, and 760 cm⁻¹. The peaks which correlated with the hydrogen spectra appear at 340, 440, 610, 700, and 770 cm⁻¹, in reasonably good agreement with the values inferred from the hydrogen spectrum. The additional peaks at lower energy in the deuteride spectra are also observed in the hydride spectra. The origin of these peaks is not currently understood, but some possibilities exist: acoustic phonons from the Pu atoms or crystal fields in the deuterides/hydrides. We are acquiring a lattice dynamics code to help us understand the "local" vibrational modes of the hydrogen/deuterium.</p>		

Experiment report (continued):

This figure shows the inelastic incoherent spectrum for $\text{PuH}_{2.33}$. Data are fit with five peaks at 550 (69), 595 (74), 804(100), 962(1120), and 1091 (136) cm⁻¹ (meV).

This figure shows the inelastic incoherent spectrum for $\text{PuH}_{2.70}$. Data are fit with five peaks at 537 (67), 604 (75), 830(104), 962(120), and 1073 (134) cm⁻¹ (meV).

This figure shows the inelastic incoherent spectrum for $\text{PuD}_{2.33}$. Data are fit with seven peaks at 230 (30), 293 (37), 340 (43), 440 (55), 610 (77), 700 (88), and 770 (96) cm⁻¹ (meV). The broad peak entering the figure from the right corresponds to some background arising from the sample, but is probably not due to a vibrational mode from the deuterium.

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- [1] R. N. R. Mulford, and G. E. Sturdy, J. Am. Chem. Soc. **77** (1955) 3449.
- [2] J. A. Goldstone, J. Eckert, P. M. Richards, and E. L. Venturini, Physica **136B** (1986) 183.
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- [4] P. P. Parshin, M. G. Zemyanov, M. E. Kost, A. Yu. Rumantsev, and N. A. Chernoplekov, Sov. Phys. Solid State **22**, (1980) 275.

Instrument used: <i>(please type)</i>	Local contact:	Proposal number: <i>(for LANSCE use only)</i>
FDS	J. Eckert	900315
Title: IINS Study of Metal-Ammonia Solutions Trapped in TiS_2		Report received: <i>(for LANSCE use only)</i> 3/14/91
Authors and affiliations:		
E. W. Ong	Arizona State University	
J. Eckert	LANSCE	
W.S. Glaunsinger	Arizona State University	
Experiment report:		
<p>Vibrational spectra were obtained for a strontium-ammonia and barium-ammonia intercalate of titanium disulfide (host). These compounds have stoichiometries conforming to the formula: $(\text{NH}_3)_u[\text{M}^{2+x}(\text{NH}_3)_{3x}](\text{NH}_4^+)_{0.25-2x}\text{TiS}_2^{-0.25}$. Evidence for the existence of nearly planar, 3-fold alkaline earth-ammonia complexes residing within the van der Waals gaps of this host has been reported recently.¹ This study is a continuation of experiments performed in the last run cycle (Exp. no. D-37). In that experiment, calcium-ammonia complexes were studied by changing the calcium concentration in the intercalates ($x=0.032$, 0.065, and 0.099). From that systematic variation, we found that "rocking" and "wagging" modes associated with the complexed ammonia molecule have energies near 167 cm^{-1} and 470 cm^{-1}. These probably correspond to the in-plane and out-of-plane wagging respectively. In the present experiment the cation was systematically changed (from Ca^{2+} to Sr^{2+} to Ba^{2+}), but the cationic concentration was kept constant at $x = 0.10$. The finding from this experiment is that the energy of the torsional modes systematically shifted to lower values as the cation "size" was increased. The high energy torsional mode found for the Ca^{2+}, Sr^{2+}, and Ba^{2+} compounds is located at 470 cm^{-1}, 460 cm^{-1}, and 425 cm^{-1}, respectively. This confirms our hypothesis that the ion-dipole interaction between the cation and ammonia grows weaker as the cation becomes bigger, due to the weaker electrostatic field around the larger cation. Previous energetics studies performed using Differential scanning calorimetry did not have the required energy resolution to differentiate between the complexes of these cations. The energy of modes associated with the uncomplexed ammonia in the compound, at 300 cm^{-1} and 320 cm^{-1}, were not appreciably effected by the cations.</p>		

Experiment report *(continued)*:

To further establish the universality of the formation of alkaline earth-ammonia complexes in the lamellar TS_2 hosts, a calcium-ammonia intercalate of tantalum disulfide was investigated. The modes associated with the complexed ammonia in this compound were found to have energies similar to those found in TiS_2 .

References:

1. On the Existence of Metal-Ammonia Solvation Complexes in Lamellar Titanium Disulfide, E.W. Ong, M.J. McKelvy, L.A. Dotson and W.S. Glaunsinger, Chem. of Mater. **3(1)**, 17 (1991).

Instrument used: <i>(please type)</i> FDS	Local contact: Juergen Eckert	Proposal number: <i>(for LANSCE use only)</i> 900702
Title: Nickel hydroxides from battery plates		Report received: <i>(for LANSCE use only)</i>

Authors and affiliations:

Lisa Diebolt, Arizona State University and MST - 4, LANL
 Juergen Eckert, LANSCE, LANL
 Ravi Varma, MST - 4, LANL
 Margaret Reid, NASA Lewis Research Center, Cleveland, Ohio

Experiment report:

We have carried out inelastic neutron scattering (INS) studies on several samples of nickel hydroxide from cycled battery plate materials in an effort to determine the importance of lattice incorporated water on the battery activity. The samples were carefully dehydrated in order to remove all intercalated water. INS spectra were collected at low temperatures on the FDS instrument at the Los Alamos Neutron Scattering Center. For reference we also obtained the spectrum from a sample of pure β -phase $\text{Ni}(\text{OH})_2$. Examples of the INS data on battery plate materials and pure β - $\text{Ni}(\text{OH})_2$ are shown in the figure below. The most prominent features in the spectra are therefore easily identified ¹: the region around 900 cm^{-1} contains $\delta(\text{OH})$; at 654 cm^{-1} we observe $\delta(\text{O-Ni-OH})$ and at 435 cm^{-1} $\nu(\text{Ni-OH})$. While it is apparent by inspection that the amount of β -phase varies in the battery plate materials, a number of more subtle changes can also be observed and highlighted with the aid of sample difference spectra between those from cycled battery plate material and β -phase $\text{Ni}(\text{OH})_2$.

Analysis of these spectra in detail is complicated by the fact that a number of different phases (α - $\text{Ni}(\text{OH})_2$, β - $\text{Ni}(\text{OH})_2$, β - and γ - NiOOH) are likely to coexist in the battery materials, and their relative proportions are known to change with cycling history. There are also additional protons in the lattice, possibly in the form H_3O^+ as well as lattice trapped water.

The differential spectra (relative to the β -phase material) reveal what are likely to be the hindered librational motions of lattice incorporated water at approximately 550, 710 and 1030 cm^{-1} . We may also identify several bands in Fig. 1 whose intensities are markedly affected by cycling history. These include a band at about 485 cm^{-1} , a second

Experiment report (continued):

component at about 670 cm^{-1} to the peak identified as $\delta(\text{O-Ni-OH})$ in the β -phase, shoulders at 780 cm^{-1} and at 950 cm^{-1} that are very strongly affected by cycling, as well as several features in the range between 1000 and 1300 cm^{-1} . Detailed evaluation of these spectra is in progress. However, it is clear that more reference spectra on the various crystalline component phases are needed to reach firm conclusions on the current set of experiments. Nonetheless, the present data do demonstrate at this early stage of our investigations that IINS may be an extremely useful tool in the microscopic analysis of the function of battery plate materials.

Fig. 1 Vibrational spectra obtained on the FDS from β -phase and battery plate nickel hydroxides.

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2. P. V. Huong and B. Desbat, *J. Raman Spectrosc.* **2**, 373 (1974).

Instrument used: <i>(please type)</i> FDS	Local contact: Juergen Eckert	Proposal number: <i>(for LANSCE use only)</i> 900705
Title: Molecular Hydrogen Complexes of Fe and Ru		Report received: <i>(for LANSCE use only)</i> 2/1/91
Authors and affiliations: Juergen Eckert, LANSCE Claudio Bianchini, Istituto per la Studio della Stereochimica, C.N.R., Firenze, Italia Alberto Albinati, Università di Milano, Italia		
Experiment report: <p>We are continuing our efforts to elucidate the factors that control the binding of the unique dihydrogen ligand in metal complexes. For example, it is generally observed that metal-ligand bond strength increases as one compares compounds going down a transition metal group in the periodic table. This seems to be the case for the newly discovered dihydrogen ligands in the series W, Mo and Cr in the sense that the thermal stability (to loss of the H₂ ligand) decreases in this direction. Furthermore, the barrier heights to dihydrogen rotation determined by neutron scattering studies [1,2] for these complexes follow the same trend. The reason for this appears to be that this barrier has its origin mainly in the direct electronic metal-dihydrogen interaction [1].</p> <p>In a series of experiments (mainly solution NMR) on the complexes [MH(η^2-H₂)(dppe)₂]BF₄ where M = Fe, Ru and Os Morris and collaborators [3] have shown that Ru seems to present an exception to the above trend, i.e. the Ru complexes consistently showed weaker M-H interaction than the Fe counterparts.</p> <p>We have therefore undertaken the study of two different Fe- and Ru-dihydrogen complexes with a cis-hydride and the tripodal ligand PP₃, [MH(η^2-H₂)PP₃]BPh₄, where M = Fe, Ru and PP₃ = P(CH₂CH₂PPh₂)₃ [4]. The "blanks" used to subtract the ligand (other than H₂) vibrations had dinitrogen ligands instead. Experiments were also carried out on the cold neutron time-of-flight spectrometer IN5 at the</p>		

Experiment report (continued):

Institut Laue-Langevin to measure the rotational ground state tunnel splitting of the dihydrogen ligand. The results of these experiments showed the same trend as for the diphos-complexes of Morris, viz. the Ru-compound was found to have a significantly lower barrier to H₂ rotation than the Fe analog. In addition, we have collected vibrational data on the FDS for both the Fe- and Ru-dihydrogen complexes, but only the "blank" for the former because of poor reliability of the source in the last run cycle of 1990. The difference spectrum is shown in the figure below. While analysis of these data in conjunction with the tunneling measurements is still in progress, it is apparent that the dihydrogen torsion can be assigned at 260/276 cm⁻¹, by far the strongest peak in the spectrum. Several other peaks are discernible, including the remaining two Fe-(H₂) deformation modes. A preliminary rotational barrier calculation yields a value of approximately 1.8 kcal/m with about 10% admixture of a fourfold component. Further experiments on this series of metal complexes are clearly necessary in order to arrive at an understanding as to why Fe appears to be a better backdonor than Ru (i.e. one possible reason for the higher barrier height).

References:

1. J. Eckert, G. J. Kubas, J. H. Hall, P. J. Hay and C. M. Boyle, J. Am. Chem. Soc. **112**, 2324 (1991)
2. J. Eckert, G. J. Kubas and R. White (unpublished)
3. M. T. Bautista, E. P. Capellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella, and J. Zubkorowski, J. Am. Chem. Soc. (in press).
4. C. Bianchini, M. Peruzzini and F. Zanobini, J. Organomet. Chem. **354**, C19 (1988),

Instrument used: <i>(please type)</i> FDS	Local contact: Jurgen Eckert	Proposal number: <i>(for LANSCE use only)</i> 900706
Title: How pressure affects vibrational coupling in para-nitroaniline		Report received: <i>(for LANSCE use only)</i> 1/25/91
Authors and affiliations: Susanna Johnson, LANSCE (LANL) Jürgen Eckert, LANSCE (LANL) Basil Swanson, INC-4 (LANL) Joe Thompson, P-10 (LANL)		
Experiment report: <p>We have obtained spectra of para-nitroaniline (pNA) at ambient pressure and at about 15 kbar as part of our program to investigate intermolecular and intramolecular vibrational coupling in high explosives, specifically the insensitive high explosive triaminotrinitrobenzene (TATB).¹ Understanding the detonation mechanism in high explosives at a microscopic level has long been a goal of LANL. A model which describes the flow of energy in a shocked solid and the initiation of detonation has been proposed and its key feature is vibrational coupling in high explosives.² In this model, the shock excites the bulk phonons. Once the bulk phonons achieve equilibrium, the excess energy is transferred to the molecular vibrations via anharmonic coupling. The most important vibrational modes involved in such a multi-phonon up pumping mechanism are the lowest energy vibrational or "doorway" modes, such as rocking, twisting, and wagging modes of the amine (NH₂) and nitro (NO₂) groups on the benzene ring of TATB. Exactly these "doorway" modes can be measured with inelastic neutron scattering, most easily when the modes involve large displacements of one or more hydrogen atoms. The vibrational spectroscopy of TATB and related molecules versus pressure gives information on vibrational coupling versus pressure and therefore can be used to test the multi-phonon up pumping model.</p> <p>The 1 bar low temperature pNA inelastic neutron spectrum shown in Figure 1 was collected in just twenty minutes by filling a standard FDS sample container with pNA powder. In order to obtain the high pressure inelastic neutron scattering spectrum of pNA shown offset in Figure 1, we first packed about 0.2 cm³ of pNA in an aluminum capsule and added fluorinert (C₆F₁₂) as a pressure medium. Upon sealing the sample capsule, we then loaded it into a pressure cell. A beryllium copper cylinder and tungsten carbide pistons form the key components of this pressure cell. Neutron</p>		

Experiment report (continued):

shielding was placed around the cell to decrease the background signal and the cell was cooled to low temperature. The background spectrum for this high pressure run was collected at low temperature using the pressure cell with fluorinert in the aluminum capsule at 1 bar. The 1 bar and 15 kbar inelastic neutron spectra are compared in Figure 1 below. Both of the inelastic neutron spectra were processed with a program which utilizes the modern maximum entropy method to deconvolve the data.³

Figure 1. Inelastic neutron scattering spectra of pNA at ambient pressure and at 15 kbar collected with the filter difference spectrometer at LANSCE. The intensity is in arbitrary units and the 15 kbar spectrum is offset above the 1 bar spectrum for clarity.

The inelastic neutron scattering spectra of pNA are dominated by features which are due to vibrations involving large amplitude motion of one or more hydrogen atoms because hydrogen has a larger neutron scattering cross section than the other nuclei. Therefore the peaks in Figure 1 are mostly due to NH₂ modes and ring modes involving displacements of hydrogen nuclei. However, vibrations involving motion of the NO₂ group are also evident in the spectra of pNA because they couple strongly to the NH₂ modes via intermolecular hydrogen bonding (i.e. the peaks at 530 and 590 cm⁻¹ are associated with the NO₂ wag and rock, respectively). The effect of pressure on the spectrum of pNA is to shift the peaks to higher energy, to broaden some of the peaks, and to change their intensities. Modes which are most sensitive to intermolecular distances, for example the NO₂ wag around 530 cm⁻¹ and the NH₂ wag around 800 cm⁻¹, shift more with pressure than modes which are less sensitive, for example the aromatic ring deformation modes at about 240 and 490 cm⁻¹. The breadth of most of the peaks increase with increasing pressure, indicating increased vibrational coupling in pNA with pressure.

Experiment report (continued):

A striking effect of pressure is the dramatic decrease in intensity of the ring deformation mode around 490 cm^{-1} . This particular mode involves large amplitude motion of carbon atoms 1 and 4 out of the plane of the aromatic ring. A space-filling model of the pNA crystal structure is shown in Figure 2 in order to illustrate the packing of molecules in pNA crystals.⁴ Intuitively, one would expect the compressibility to be greater perpendicular to the molecular planes. If so, one might expect the intensities of modes which involve large atomic displacements perpendicular to the plane of the molecule to be suppressed when the pressure is increased. This conclusion is indeed borne out by the fact that the 490 cm^{-1} peak almost disappears with pressure; and it is further supported by the decrease in intensity with pressure of the NH_2 wagging mode found at about 800 cm^{-1} .

Figure 2. The crystal structure of pNA: a space-filling model to show how the molecules pack together. The drawing is taken directly from reference 4.

This experiment demonstrates the feasibility of low temperature inelastic neutron scattering up to pressures of about 15 kbar, and how shielding improves the resolution of such spectra. Furthermore, if enough sample is available, high resolution inelastic neutron scattering spectra can be obtained with the FDS in a very short time (about 20 minutes). The effect of 15 kbar pressure on the vibrational modes of pNA is to increase their energy, to increase the coupling between modes, and to suppress modes involving displacements perpendicular to the molecular plane.

References:

1. S. K. Satija, B. I. Swanson, J. Eckert and J. A. Goldstone, "High Pressure Raman Scattering and Inelastic neutron scattering studies of TATB", *J. Phys. Chem.*, accepted December 1990.
2. D. D. Dlott and M. D. Fayer, "Shocked Molecular Solids: Vibrational Up Pumping, Defect Hot Spot Formation, and the Onset of Chemistry", *J. Chem. Phys.*, submitted.
3. D. S. Sivia, P. Vorderwisch and R. N. Silver, "Deconvolution of Data from the Filter Difference Spectrometer: from Hardware to Maximum Entropy", *Nucl. Instr. and Meth.*, **A290**, pp 492-498 (1990).
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Instrument used: <i>(please type)</i> FDS	Local contact: Jürgen Eckert	Proposal number: <i>(for LANSCE use only)</i> 900606.1
Title: The effect of pressure on vibrational coupling in para-nitroaniline		Report received: <i>(for LANSCE use only)</i> 2/7/91
Authors and affiliations: Susanna Johnson, LANSCE (LANL) Jürgen Eckert, LANSCE (LANL) Basil Swanson, INC-4 (LANL) Joe Thompson, P-10 (LANL)		
Experiment report: <p>We have obtained spectra of p-nitroaniline (pNA) at ambient pressure and at about 15 kbar as part of our program to investigate intermolecular and intramolecular vibrational coupling in high explosives, specifically the insensitive high explosive triaminotrinitrobenzene (TATB).¹ Understanding the detonation mechanism in high explosives at a microscopic level has long been a goal of LANL. A model which describes the flow of energy in a shocked solid and the initiation of detonation has been proposed and its key feature is vibrational coupling in high explosives.² In this model, the shock excites the bulk phonons. Once the bulk phonons achieve equilibrium, the excess energy is transferred to the molecular vibrations via anharmonic coupling. The most important vibrational modes involved in such a multi-phonon up pumping mechanism are the lowest energy vibrational or "doorway" modes, such as rocking, twisting, and wagging modes of the amine (NH₂) and nitro (NO₂) groups on the benzene ring of TATB. Exactly these "doorway" modes can be measured with inelastic neutron scattering, most easily when the modes involve large displacements of one or more hydrogen atoms. The vibrational spectroscopy of TATB and related molecules versus pressure gives information on vibrational coupling versus pressure and therefore can be used to test the multi-phonon up pumping model.</p> <p>The 1 bar low temperature pNA inelastic neutron spectrum shown in Figure 1 was collected in just twenty minutes by filling a standard FDS sample container with pNA powder. In order to obtain the high pressure inelastic neutron scattering spectrum of pNA shown offset in Figure 1, we first packed about 0.2 cm³ of pNA in an aluminum capsule and added fluorinert (C₆F₁₂) as a pressure medium. Upon sealing the sample capsule, we then loaded it into a pressure cell. A beryllium copper cylinder and tungsten carbide pistons form the key components of this pressure cell. Neutron</p>		

Experiment report (continued):

shielding was placed around the cell to decrease the background signal and the cell was cooled to low temperature. The background spectrum for this high pressure run was collected at low temperature using the pressure cell with fluorinert in the aluminum capsule at 1 bar. The 1 bar and 15 kbar inelastic neutron spectra are compared in Figure 1 below. Both of the inelastic neutron spectra were processed with a program which utilizes the modern maximum entropy method to deconvolute the data.³

Figure 1. Inelastic neutron scattering spectra of pNA at ambient pressure and at 15 kbar collected with the filter difference spectrometer at LANSCE. The intensity is in arbitrary units and the 15 kbar spectrum is offset above the 1 bar spectrum for clarity.

The inelastic neutron scattering spectra of pNA are dominated by features which are due to large amplitude vibrations involving one or more hydrogen atoms because hydrogen has a larger neutron scattering cross section than the other nuclei. Therefore the peaks in Figure 1 are mostly due to NH₂ modes and ring modes involving displacements of hydrogen nuclei. The effect of pressure on the spectrum of pNA is to shift the peaks to higher energy, to broaden some of the peaks, and to change their intensities. It appears that the modes which are most sensitive to intermolecular distances, for example the NH₂ torsion around 400 cm⁻¹ and the NH₂ wag around 600 cm⁻¹, shift more with pressure than modes which are less sensitive, for example the aromatic ring deformation mode at about 500 cm⁻¹. The breadth of most of the peaks increase with increasing pressure, indicating increased vibrational coupling in pNA with pressure.

A striking effect of pressure is the dramatic decrease in intensity of the ring deformation mode around 500 cm⁻¹. This particular mode involves large

Experiment report (continued):

amplitude motion of carbon atoms 1 and 4 out of the plane of the aromatic ring. A space-filling model of the pNA crystal structure is shown in Figure 2 in order to illustrate the packing of molecules in pNA crystals.⁴ Intuitively, one would expect the compressibility to be greater perpendicular to the molecular planes. If so, one might expect the intensities of modes which involve large atomic displacements perpendicular to the plane of the molecule to be suppressed when the pressure is increased. This conclusion is further supported by the decrease in intensity with pressure of the NH₂ wagging mode around 800 cm⁻¹.

Figure 2. The crystal structure of pNA: a space-filling model to show how the molecules pack together. The drawing is taken directly from reference 4.

This experiment demonstrates the feasibility of low temperature inelastic neutron scattering up to pressures of about 15 kbar, and how shielding improves the resolution of such spectra. Furthermore, if enough sample is available, high resolution inelastic neutron scattering spectra can be obtained with the FDS in a very short time (about 20 minutes). The effect of a pressure of 15 kbar on the vibrational modes of pNA is to increase their energy, to increase the coupling between modes, and to suppress modes involving displacements perpendicular to the molecular plane.

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**Constant-Q
Spectrometer
(CQS)**

Constant-Q Spectrometer (CQS)

The Constant-Q Spectrometer (CQS) is an inelastic scattering instrument designed for the study of collective atomic vibrations and analogous magnetic phenomena waves. A pulsed white beam of neutrons from the source illuminates a sample, which is normally a single crystal. After scattering at the sample, the neutrons are intercepted by a large germanium or copper analyzer that diffracts the neutrons into an array of 96 detectors. The essence of the method is to measure the change in neutron energy when scattering takes place. This is achieved by the analyzer in conjunction with the conventional time-of-flight technique.

The CQS has two principal features: first, the rich higher-energy spectrum at a pulsed source makes this machine suitable for the study of higher-energy collective excitations (50 meV and above), and second, the mapping capability of the instrument makes it suitable for survey work.

Instrument Details

Detectors	Movable bank of 96 ^3He (1.3 cm diameter), 0.57° apart
Detector range	$10 - 70^\circ$
Energy-transfer resolution	4 - 10%
Analyzer planes	Ge (hh), Cu (hh)
Beam size at sample	2.5 cm wide x 5 cm high
Moderator	Chilled water at 10°C
Sample environment	Closed cycle refrigerator
Experiment duration	~1 week

Robert Robinson, instrument scientist

Eric Larson, instrument technician

New Instruments

PHAROS

10 μeV Spectrometer

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. 1a) and consists of an evacuated, shielded flight path for low-angle scattering ($1^\circ < \theta < 10^\circ$). The spectrometer is suitable for low-angle studies such as neutron Brillouin scattering and magnetic excitations.

Phase II of the construction will be completed

by April 1993 (Fig. 1b). The spectrometer will then 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 state, magnetic excitations, momentum distributions, crystal-field levels, chemical spectroscopy, and measurements of $S(Q, \omega)$ in disordered systems. In addition, the low-angle detectors can be used 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 (April 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

10 μeV Spectrometer

The 10 μeV spectrometer is a new time-of-flight backscattering instrument for quasielastic and high-resolution inelastic spectroscopy. This instrument will be installed in 1993. The incident neutron energy is measured by time of flight through a long incident flight path of 30 m. The energy of the scattered neutrons (about 2 meV) is determined from backscattering from single crystals of graphite or silicon. The instrument is to be installed on flight path 11, which is one of the three flight paths viewing the liquid-hydrogen moderator. The combination of this moderator and neutron beam guides between the moderator and the sample maximizes the neutron flux incident on the sample in the energy region between 1 meV and 4 meV.

The new spectrometer is designed for studies of diffusion and low-frequency dynamics. Examples of future experiments are reorientational and tunneling motions in molecular crystals, motion of molecules on surfaces, and dynamics of simple biological systems.

Instrument Details

Quasielastic scattering:

Final energy	2 meV
Q range	$0.035 \text{ \AA}^{-1} - 2 \text{ \AA}^{-1}$
Resolution	10 μeV

Inelastic scattering:

Energy transfer range	0 - 50 meV
Q range	$1 \text{ \AA}^{-1} - 10 \text{ \AA}^{-1}$
Resolution	1% of incident energy (FWHM)
Moderator	Liquid H ₂ at 20 K
Sample size	3 cm x 3 cm

Torben Brun, instrument scientist
Ross Sanchez, instrument technician

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