Conf-9410115--1

LA-UR- 94 - 3422

DISCLAIMER

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

Title:

HIGH PRESSURE NEUTRON POWDER DIFFRACTION AT LANSCE

Author(s):

ROBERT VON DREELE

Submitted to:

Proceedings of the International Seminar on Neutron
Scattering at High Pressures, Dubna, Russia, 5-7 Oct 94

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *EP*

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Form No. 836 R5
ST 2629 10/91

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

High Pressure Neutron Powder Diffraction at LANSCE

Robert B. Von Dreele, LANSCE, MS H805, Los Alamos National Laboratory, Los Alamos, NM 87545 USA.

Abstract:

By making use of the recently developed "Paris-Edinburgh" high pressure cell, we have successfully performed neutron powder experiments to 10GPa at ambient temperature. Results for the structural compression of the high T_c 1223-Hg superconductor to 9.2GPa, the compression and possible hydrogen bond formation in brucite, $Mg(OD)_2$, to 9.3GPa, and the molecular reorientation in nitromethane to 5.5GPa will be presented.

Introduction:

Due to its very short incident flight path (9m), the High Intensity Powder Diffractometer (HIPD) at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) provides a very intense incident neutron beam so that standard "little finger" sized samples frequently scatter sufficiently strongly so that data collection times are often much less than one hour. Thus, it is possible to obtain diffraction patterns from considerably smaller samples and in the very restricted geometry of the "Paris-Edinburgh" (1) 10GPa high pressure apparatus. This has enabled us to examine with some detail various structural changes with pressure particularly those involving changes in hydrogen atom positions. Some of our recent results which demonstrate these capabilities are discussed below.

Small Sample Example:

A recent study (2) of the crystal structures of some high oxidation state metal fluorides demonstrates the small sample capabilities of HIPD. The risks involved in synthesizing and handling these very reactive materials were the driving force in doing the work with small samples rather than using standard 5gm samples. For example, a four hour neutron powder diffraction run (Fig. 1) from a 100mg sample of AuF_3 contained in a sealed 2mm diameter thin-wall quartz capillary yielded data gave a satisfactory Rietveld refinement of the crystal structure (Fig. 2). A similar result was also obtained in this study from a 100mg sample of the even more reactive AgF_3 , one of the starting materials for the synthesis of KrF_2 .

High Pressure Examples:

Brucite: In one our first uses of the Paris-Edinburgh cell for TOF neutron powder diffraction at LANSCE, we examined the pressure induced structural changes in the prototypical water bearing mineral, brucite ($Mg(OD)_2$) (3). Brucite is a layer structure consisting of MgO rock salt layers separated by OH containing interlayer spaces. There is no hydrogen bonding between the layers in this material under ambient conditions; upon heating it readily decomposes to MgO and water. However, under sufficient pressure (~ 4 GPa) brucite is stable to much higher temperatures ($\sim 1000^\circ C$). In our study to 9.3GPa we found that the hydrogen atom is displaced with increasing pressure forming a hydrogen bond to oxygen in the adjacent MgO layer (Fig. 3). It is this hydrogen bond formation that probably accounts for the increased stability of this material with pressure.

Hg-1223 Superconductor: The recently discovered $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ ($n=1,2$ and 3) high T_c oxide superconductors have been shown to exhibit some of the highest superconducting transition temperatures. In particular, the $n=3$ material, Hg-1223

(Fig. 4), has the highest transition temperature, 135K, which has been shown to increase to above 150K at high pressure (>10GPa) (4). We examined by neutron powder diffraction a sample of this material in the Paris-Edinburgh press at 4.0 (Fig. 5) and 9.2GPa to see the structural changes that accompany this increase in T_c . Most evident was that the c-axis was ~2 times more compressible than the a-axis and that the Hg-O2 bond showed a dramatic shortening with pressure (Fig. 6). Any change in the apical Cu2-O2 distance with pressure was less evident.

Nitromethane: Based on some Raman studies (5) at high pressure (~2GPa), nitromethane has been thought to decompose by a mechanism involving a rotation about the C-N bond followed by dissociation of a hydrogen ion to form the aci ion $[\text{CH}_2\text{NO}_2^-]$. A subsequent study (6) by single crystal diffraction in a diamond anvil cell showed that the rotation seems to occur at ~3.5GPa but no evidence was found for significant dissociation. As the x-ray work was unable to give very definitive locations for the hydrogen atoms, we embarked on this neutron powder diffraction study using the Paris-Edinburgh cell. The sample of d3-nitromethane was mixed with aerogel and NaCl to form a thick paste which was loaded into the sample volume of the cell. Aerogel is an extremely low density (~0.17gm/cc) form of amorphous silica; we hoped that its extremely large surface area would promote formation of a nitromethane powder and prevent growth of large single crystals. Earlier attempts had yielded powder diffraction patterns which were evidently the result from a few large crystal grains. In addition, the paste was readily handled during the loading procedure. Diffraction data were then obtained at a range of pressures to 5.5GPa. Fig. 7 shows the diffraction pattern obtained at 0.6GPa. Despite contamination of this pattern by the tungsten carbide anvils, which had been inadequately shielded in this experiment; an initial Rietveld refinement of the structure of nitromethane from this data yielded atomic positions essentially identical with those obtained in the single crystal x-ray study at the same pressure (Table 1). This refinement was augmented by the addition of a set of "observed" interatomic distances for nitromethane.

Table 1. Atom positions for nitromethane at 0.6GPa from single crystal x-ray and neutron powder diffraction studies

Atom		x	y	z
C	(x)	0.123(3)	1.053(4)	0.384(2)
	(n)	0.1237(25)	1.0593(27)	0.3933(23)
N	(x)	0.361(2)	0.915(3)	0.381(1)
	(n)	0.3443(24)	0.9074(19)	0.3884(14)
O1	(x)	0.515(2)	0.938(2)	0.487(1)
	(n)	0.5285(24)	0.9464(33)	0.4738(24)
O2	(x)	0.387(2)	0.792(3)	0.273(1)
	(n)	0.3691(24)	0.8032(29)	0.2683(22)

In neither study were the hydrogen atoms located at 0.6GPa from difference Fourier maps; apparently the methyl group undergoes essentially free rotation at this pressure. Extension of this refinement procedure including the "soft constraints" of interatomic distances did not succeed with the remaining data sets taken at higher pressure. Successful Rietveld refinements were obtained at all pressures to 5.5GPa by considering the nitromethane to be composed of two linked rigid bodies with fixed internal dimensions. One rigid body consisted of the NO₂ group and the other was the CD₃ with the D atoms disordered over two orientations. This description reduced the number of "free" variables for the nitromethane molecule from 32 to 8 which greatly stabilized the

least-squares refinement. Thus, the nitromethane is described by three rotations and three translations of the rigid body and one additional torsional rotation about the CD₃ - NO₂ bond. In Figure 8 the variation of these seven rigid body parameters with pressure are shown. Figure 9 shows drawings of the unit cell for d₃-nitromethane at 0.6GPa and 5.5GPa. Evidently, the nitromethane molecule does not change its orientation or position relative to its neighbors very much with increasing pressure. The disordered D-atom positions do not seem to move much either with pressure. The refinements included a fractional occupancy for the two sets of D-atoms; it varied from near 50/50 to about 20/80 with increasing pressure. Thus, it appears that in d₃-nitromethane the methyl remains disordered even at 5.5GPa in contrast with h₃-nitromethane although one orientation may predominate at the highest pressure. In Figure 10 the equation of state data from both studies are shown. The result of fits to a Murnaghan equation

$$P = \frac{B_0}{B_0'} \left[\left(\frac{V_0}{V} \right)^{B_0'} - 1 \right]$$

are shown in Table 2. Evidently the d₃-nitromethane is somewhat less compressible than the undeuterated material particularly at the highest pressures.

Table 2 Fits of volume EOS data for nitromethane and d₃-nitromethane

	CH ₃ NO ₂	CD ₃ NO ₂
V ₀	292.7(28)	296.2(52)
B ₀	7.0(14)	5.7(17)
B ₀ '	5.8(8)	7.8(9)

Acknowledgements:

This work was done in collaboration with J. Jorgenson of ANL, J. Parise of SUNY, StonyBrook, NY and D. Schiferl of LANL and is supported by the Division of Basic Energy Sciences of the USDOE.

References:

- (1) Nelmes, R.J., Loveday, J.S., Wilson, R.M., Besson, J.M., Pruzan, P., Klotz, S. and Hull, S. (1993). Phys. Rev. Letters **71**, 1192-1195.
- (2) Zemva, B., Lutar, K., Jesih, A., Casteel, W.J. Jr., Wilkinson, A.P., Cox, D.E., Von Dreele, R.B., Borrmann, H. and Bartlett, N. (1991). Jour. Am. Chem. Soc. **113**, 4192-4198.
- (3) Parise, J.B., Leinenweber, K., Weidner, D.E., Tan, K., and Von Dreele, R.B. (1994). Am. Mineral. **79**, 193-196.
- (4) Hunter, B.A., Jorgensen, J.D., Wagner, J.L., Radaelli, P.G., Hinks, D.G., Shaked, H., Hitterman, R.L., and Von Dreele, R.B. (1994). Physica **C221**, 1-10.

(5) Engelke, R. , Schiferl , D. , Storm, C.B. and Earl, W.L. (1988). J. Phys. Chem. **92**, 6815-6819.

(6) Cromer, D.T., Ryan, R.R., and Schiferl, D. (1985). J. Phys. Chem. **89**, 2315-2318.

Figures:

23-SEP-94 09:35:35

Figure 1. Portion of the fitted TOF pattern from 100mg of AuF₃. Observed data (+) has been normalized by the incident intensity distribution.

Figure 2. Refined crystal structure of AuF₃ from Rietveld refinement of TOF data.

Figure 3. The structure of brucite, $\text{Mg}(\text{OD})_2$, at high pressure. Hydrogen atoms are shown disordered and displaced to form hydrogen bond to adjacent MgO layer. The changes in $\text{OD}\cdots\text{O}$ angle and $\text{D}\cdots\text{O}$ distance with pressure are also shown.

Figure 4. Crystal structure of Hg-1223 high Tc oxide superconductor at 4.0 GPa.

Figure 5. TOF neutron powder diffraction data for Hg-1223 high T_c oxide superconductor at 4.0 GPa. The observed data have been normalized by the incident intensity; the computed background from the Rietveld refinement has been subtracted. The EOS of the major contaminant, CaO, was used as the internal pressure calibrant.

Figure 6. Compressibility and apical Hg-O and Cu-O bond lengths in Hg-1223 high T_c oxide superconductor to 9.2 GPa.

Figure 7. Powder diffraction data from d3-nitromethane at 0.6 GPa. Observed and calculated are shown as crosses and solid line, respectively. A difference curve is also shown.

Figure 8. Rigid body parameters for d3-nitromethane as a function of pressure are shown. The four angles are shown on the left and the three translations are shown on the right.

Figure 9. Unit cell drawings of d₃-nitromethane at 0.6GPa and 5.5GPa. The d-atoms are shown disordered over two sites. In both drawings the c-axis is up the paper and the view is down the a-axis.

Figure 10. Volume equation of state data for nitromethane. Open circles are data from single crystal data of Cromer, et. al. (7) and filled circles from this study. Curves are from a fit to a Murnaghan equation.