

STRUCTURAL STUDIES AT HIGH PRESSURE USING
TIME-OF-FLIGHT NEUTRON POWDER DIFFRACTION

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**Structural Studies at High Pressure
Using Time-of-Flight Neutron Powder Diffraction**

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ABSTRACT

Time-of-flight neutron powder diffraction offers unique capabilities for structural studies at high pressure. Scientific applications have included studies of compression mechanisms, new high-pressure structures, and phase transitions.

Neutron powder diffraction (NPD) techniques have been used for a number of years to study structural properties of samples in high pressure environments. The success of this method largely stems from the high penetrating power of the neutron, allowing a number of different pressure cell designs to be employed. Although many experiments have been done by the constant-wavelength technique on reactor neutron sources, the constant-angle time-of-flight (TOF) technique, used originally at reactors and more recently at pulsed neutron sources, has proven most effective because of the ability to completely mask unwanted scattering from the pressure cell (Jorgensen, 1988). Due to space limitations, this brief review will focus on high-pressure structural studies done by the TOF NPD technique, largely pioneered at Argonne National Laboratory.

Pressure cell designs differ according to the maximum pressure. Two designs are most commonly used (Jorgensen, 1988). Supported aluminum oxide cells take advantage of the high compressive strength of aluminum oxide. A hollow cylinder of aluminum oxide is supported by a steel binding ring assembled such that, at zero sample pressure, the aluminum oxide is under maximum compression. As the sample pressure is increased, the compression in the aluminum oxide decreases, eventually passing through zero. The cell fails when the aluminum oxide reaches its tensile limit, typically corresponding to a sample pressure of 30-50 kbar depending on cell dimensions and geometry. The other popular design is a relatively standard helium gas pressure cell, typically capable of pressures to about 8 kbar. Gas cells offer the advantages of precise pressure control and measurement, perfectly hydrostatic conditions, and large sample volume.

TOF NPD studies at high pressure have concentrated mainly in three areas: (1) compression mechanisms, (2) determination of structures which exist only at high pressure, and (3) pressure-induced phase transitions. Brief examples which illustrate the strengths of the technique in each area will be discussed.

Compression mechanism studies have the goal of understanding the response of individual bond lengths and angles to applied pressure. Such information is important in geophysics and also in understanding the mechanical properties of technologically useful materials. Perhaps the best-known example of such work is the study of compression mechanisms in the isostructural alpha-quartz forms of SiO_2 and GeO_2 . (Jorgensen, 1978). In SiO_2 , compression results from a cooperative rotation of nearly rigid SiO_4 tetrahedra, while in GeO_2 the analogous rotation has already proceeded so far at ambient pressure that compression must proceed by distorting the tetrahedral angles. Bond-length changes are very small in both cases. This behavior forms the basis for understanding compression in a wide range of ceramics, such as Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$ (Cartz and Jorgensen, 1981), and minerals with framework structures.

New structures determined recently at high pressure include KNO_3 -IV at 3.6 kbar (Worlton et al., 1986) and ND_4F -II at 4.7 kbar (Lawson et al., 1989). In both cases, TOF NPD data taken in a helium gas cell were of high enough quality to allow the unknown structures to be indexed and the space groups determined. Full structure refinements were then done by the Rietveld method. Fig. 1 shows the Rietveld refinement profile for a mixture of KNO_3 -II and KNO_3 -IV at 3.06 kbar, where, because the transformation is first order, the two phases coexist even though the pressure is perfectly hydrostatic (Worlton, Jorgensen, and Kleb, unpublished). ND_4F -II with 24 molecules in a 1024 \AA^3 hexagonal unit cell is one of the most complex

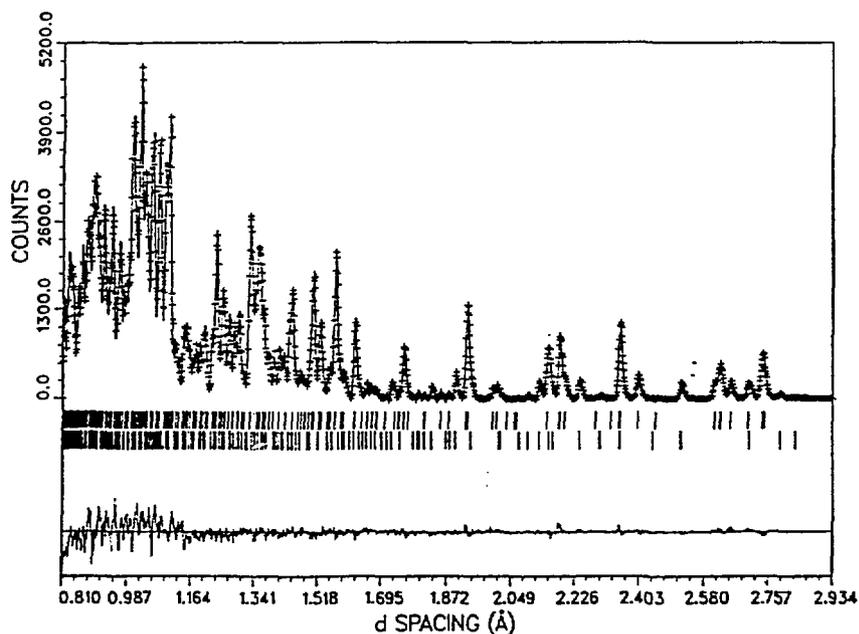


Fig. 1. Rietveld refinement profile for a mixture of KNO_3 -II and KNO_3 -IV at 3.06 kbar and 295 K. Tick marks below the plot mark the positions of allowed peaks for the two phases.

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structures to be solved from high pressure data. Other well-known structural determinations include studies of D₂O ice-VII at 26 kbar (Jorgensen and Worlton, 1985) and ice-VIII at 28 kbar (Jorgensen et al., 1984) for which the unit cells were known from x-ray studies, but the positions of the light D atoms could only be determined by neutron diffraction.

Studies of phase transitions have included electronic transitions such as the Lifshitz transition in InBi (Jorgensen and Clark, 1980), Martensitic transformations as in lithium metal (Smith, Berliner, and Jorgensen, 1989), and soft-mode transitions as in NiF₂ (Jorgensen, Worlton and Jamieson, 1978) and ReO₃ (Jorgensen et al., 1986). The studies of soft-mode transitions offer the best example of the unique capability for neutron powder diffraction to give accurate Bragg intensities from which structural parameters, such as bond lengths and angles, can be determined. Thus, for both NiF₂ and ReO₃ it was possible to accurately measure the pressure dependence of the appropriate order parameters for the transitions, e.g., the rotation angle of ReO₆ octahedra in the case of ReO₃.

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