High-Pressure Single-Crystal Neutron Diffraction (to 20 kbar) Using a Pulsed Source: Preliminary Investigation of Tl$_3$PSe$_4$

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Abstract
A new technique is described for performing high-pressure single-crystal neutron diffraction [up to 20 kbar (2GPa) at room temperature], using a BeCu pressure cell, an area detector and the Los Alamos National Laboratory pulsed neutron source. Success of this method depends on the increase in information available with a multi-wavelength pulse neutron source, a novel orientation of a cylindrically symmetric pressure cell with its axis coincident with the neutron beam and a specific crystal orientation within the pressure cell. Bragg scattering from the pressure cell is avoided and background for a given 20 is constant. For a crystal of orthorhombic or higher symmetry oriented with the incident beam passing midway between the major lattice vectors, it will be possible to refine a complete three-dimensional structure with data collected from only one pressure loading. Preliminary investigations of Tl$_3$PSe$_4$ lattice parameters (space group Pcmn) at 15(1)kbar yielded linear compressibilities ($\times$ 1000 in kbar$^{-1}$) of $K_a = 1.05(8)$, $K_b = 1.50(10)$, $K_c = 1.20(8)$. The anisotropic compressibility is explained by examination of the ambient-pressure room-temperature structure.

Introduction
X-ray diffraction studies of materials under high pressure were conducted as early as 1933 (Cohn, 1933), yet it was not until the mid to late 1970's that complete three-dimensional high-pressure structure refinements were being performed routinely on single-crystal specimens (Hazen & Finger, 1982; Adams & Martin, 1981). Application of high-pressure powder diffraction techniques using neutrons started around 1964 (Litvin & Ponyatovskii, 1964; Brugger, Bennion, Hall, 1965) while a complete high-pressure three-dimensional single-crystal data set was not refined until 1975 (Vettier & Yelon, 1975). Given the availability of X-rays over neutrons, it is not surprising that most complete high-pressure structure refinements have been performed with X-rays (Hazen & Finger, 1982). However, significant progress using single-crystal neutron diffraction techniques at high pressure has been made as is evidenced by the structure of TTF-TCNQ at 4.6 kbar, which has recently been reported (Filhol, Bravic, Gaultier, Chasseau & Vettier, 1981).

Difficulties in advancing high-pressure single-crystal diffractometry have been due to a number of factors. These include high-pressure cell technology (Hazen & Finger, 1982; Jayaraman, Hutson, McFee, Coriell & Maines, 1967; Carlile & Salter, 1978; Kalus & Alt, 1981; Brugger, Bennion, Worlton & Meyers, 1969), absorption by support materials, limitations in accessible reciprocal space imposed by the size of high-pressure apparatus, and increased background originating from containment walls and pressurizing fluids. Four-circle neutron diffractometers using monochromatic neutron sources are particularly susceptible to changes in the background since the high-pressure apparatus must be reoriented for each individual reflection.

It is the purpose of this paper to describe a technique for performing high-pressure single-crystal diffraction (up to 20 kbar) using a pulsed neutron source (Windsor, 1981) and a stationary two-dimensional area detector. Laue time-of-flight (TOF) diffraction is used (Buras, Mikke, Lebech & Leciejewicz, 1965), i.e. the crystal position is constant while wavelength is resolved. With the proper crystal orientation relative to the incident neutron beam, sufficient data for a complete three-dimensional structure refinement can be collected without changing crystal position within the pressure cell, provided the crystal is of orthorhombic or higher symmetry. We describe preliminary measurements on Tl$_3$PSe$_4$ (space group Pcmn) covering changes in lattice parameters at 15(1)kbar. Tl$_3$PSe$_4$ is one of several chalcogenide crystals that have demonstrated a shear acoustic mode with an unusually low wave velocity. Ultrasonic measurements of this mode in Tl$_3$PSe$_4$ as a function of pressure indicate a mode softening transition above 14 kbar, which is completely reversible (Fritz, Isaacs,
Gottlieb & Morosin, 1978). Attempts to observe this transition with diamond-cell X-ray techniques have, so far, been unsuccessful (Fritz, Gottlieb, Isaacs & Morosin, 1981).

Experimental

The $\text{Tl}_3\text{PSe}_4$ sample $(2 \times 2 \times 6 \text{ mm})$ was cut with an abrasive wheel so that the long axis was along the [111] direction of the orthorhombic crystal. Design for the high-pressure cell used in this study (Fig. 1) is similar to that reported by Chu (Chu, Rusakov, Huang, Early, Geballe & Huang, 1978; Jayaraman, Hutson, McFee, Coriell & Maines, 1967), and closely resembles a high-pressure cell used for powder neutron diffraction (McWhan, Bloch & Parisot, 1974). Fabricated from Beryllco 25 (Be$_{0.125}$Cu$_{0.88}$), the pressure cell was strain-hardened by pressurization to 23 kbar, after which the original 6 mm bore was machined to 6.35 mm. Epoxy was used to mount the sample on a hollow Gd pedestal, which aids in collimating the incident neutron beam and helps reduce internal (forward) scattered radiation. Hydrostatic pressure is applied to the sample by depressing a tungsten carbide piston onto the Teflon sample chamber filled with Fluorinert 77 (a non-hydrogenous fluid). Seals are made with BeCu compression rings and pressure is monitored by observation of strain on the external circumference of the pressure cell with a manganin strain gage.

The single-crystal diffractometer (SCD) at Los Alamos National Laboratory has recently been redesigned (Vergamini, Alkire & Larson, 1985). The high-pressure experiment described here utilizes the source and detection system of the new SCD. A Borkowski–Kopp type (Borkowski & Kopp, 1978) position-sensitive proportional counter filled with 2 atm (0-20 MPa) of $^3$He $+$ Xe $+$ CO$_2$ is used to detect diffracted neutrons and the detector is positioned with its center at a nominal $2\theta$ of 90°. Detector center (active area $25 \times 25 \text{ cm}$) is positioned 26-75 cm from the sample (detector-to-sample distance is variable to 50 cm) and located 45° above the horizontal plane (angular range 30 to 50°); this arrangement provides maximum flexibility for designing special environmental experiments. Neutron pulse repetition rate is at present 120 Hz and the sample-to-source distance is 7.5 m, producing a useful wavelength range of 0.75 to 4.2 Å. Each event on the detector is binned within a framework consisting of $64 \times 64$ spatial $(x, y)$ channels and a time resolution of 188 channels. The volume of reciprocal space covered by the area detector for a single setting of the crystal is referred to as a histogram.

One of the major problems associated with high-pressure diffraction (employing vertical or semi-vertical cell geometry) is shielding against Bragg scattering from the pressure-cell walls. This task is particularly difficult if an area detector is used because the shielding must terminate well outside the central pressure cell cavity. Forward and backward Bragg scattering (powder lines) from the pressure cell can only be avoided with extremely tight collimation, greatly reducing the effectiveness of an area detector. In order to optimize shielding and take advantage of the fixed crystal geometry used in TOF diffraction, the pressure cell is mounted with its axis coincident with the pulsed neutron beam (Fig. 2). Scattered neutrons exit nominally 90° to the incident beam ($2\theta$ ranges 90 ± 25°). Motion of the crystal is accomplished by...
rotating the pressure cell around the incident-beam direction. At present, the high-pressure cell is designed only for room-temperature work and is relatively light (300 g). Rotation can be accomplished by attaching the pressure cell to a cylindrical tube which slides over the section of incident-beam collimator following the fission monitor detector. Crystal position within the pressure cell is predetermined by X-ray or neutron radiographic techniques and final alignment (corresponding to a translational adjustment parallel to the incident beam) is accomplished with the aid of a precision alignment pointer attached to the detector shielding box. Additional Cd or Gd shielding is placed around the pressure cell outside the 50° cone of Bragg scattering to minimize detection of background produced by the transmitted beam.

After pressurizing the sample to 15(1) kbar, the BeCu pressure cell was removed from the pressurizing apparatus. Periodic readings of the manganin gage indicated no signs of depressurization for a period of up to one month. Nine histograms were collected with an average data collection time per histogram of 5-5 h. For this work,* rotation of the pressure cell around the incident beam collimator was done manually, employing a dial indicator attached to the cylindrical tube mount and referenced to the incident-beam collimator. Maximum positioning error is estimated to be ±0.5°. Fig. 3 illustrates the typical signal-to-noise resolution of a Bragg reflection found in a single time frame; the x direction corresponds to the 2θ direction with a resolution of approximately 0.75° (2θ) channel⁻¹.

**Results and discussion**

Time-of-flight diffraction using a multi-wavelength pulsed neutron source is significantly different from monochromatic diffraction techniques in that the crystal is stationary and individual orders of a Bragg plane all diffract neutrons to the same spot on the detector. Resolution of individual hkl intensities is possible because each solution to the Bragg equation corresponds to neutrons separated according to TOF over a fixed moderator-to-detector distance. With the addition of an area detector, each crystal setting allows measurement of all the diffracted intensity, as well as systematic absences, in a particular volume of reciprocal space (defined by the wavelength range, crystal orientation and instrument parameters). Since multiple orders of a single reflection are collected, a considerable amount of data is available that is not otherwise accessible to ordinary single-crystal techniques while employing restrictive, special environment devices, such as the high-pressure cell.

As one might expect, however, reducing freedom of motion to a single rotation does introduce restrictions on accessible reciprocal space, provided one assumes that all data must be obtained during a single pressure loading. Choice of crystal orientation within the pressure cell then becomes extremely important. To illustrate the potential for this experimental geometry, a diagram has been constructed that illustrates regions of reciprocal space accessible for a crystal oriented with the incident beam entering the crystal midway between the major lattice vectors (Fig. 4). Each semi-rectangular section represents coverage for a single histogram using the area detector. For a crystal that is of orthorhombic (or higher) symmetry, enough information is accessible to determine uniquely the space group and solve the structure. With current instrument parameters, nine histograms are required to complete coverage of accessible reciprocal space, denoted by the shaded area in Fig. 4. Because certain

*Since completion of this work, pressure-cell rotation has been automated, with 0.01° step⁻¹ resolution.

Fig. 3. Typical resolution of a Bragg reflection found in a single time frame. 188 time frames are used in each individual histogram.

Fig. 4. Projection onto a sphere representing reciprocal space showing the accessibility of data for a crystal specimen mounted with the [111] direction parallel to the incident neutron beam. Current instrument parameters require nine histograms to completely cover 360° rotation of the high-pressure cell; for clarity, only seven are shown. For orthorhombic symmetry, equivalent reflections related by mirrors located within the histogram allow data to be collected covering the shaded portion of the octant.
areas of reciprocal space are not covered, standard deviations of atom parameters will probably be slightly higher than normal.

The structure of Tl$_3$PSe$_4$ (Fig. 5) has been determined by TOF neutron diffraction at room temperature and ambient pressure (Alkire, Vergamini, Larson & Morosin, 1984) and lattice parameters are

\[
a = 9.276(1), \quad b = 11.036(2), \quad c = 9.058(1) \text{ Å.}
\]

At 15 kbar, lattice parameters were determined by least-squares refinement of 112 reflections, with lattice angles constrained to be 90°. Lattice constants are

\[
a = 9.130(4), \quad b = 10.787(4), \quad c = 8.895(3) \text{ Å, corresponding to linear compressibilities (× 1000 in kbar}^{-1})\text{ of } K_a = 1.05, \quad K_b = 1.50(10), \quad K_c = 1.20(8).
\]

The structure consists of layers situated about mirror planes normal to the b axis at y = 1/4 and y = 3/4. In each formula unit one Tl, the P and two Se atoms of the PSe$_2$\(^3\) group are situated on the mirror plane; the remaining two Tl and two Se atoms are symmetrically disposed about the plane. The latter two Tl atoms serve as the link between layers in the structure.

Explanation for the anisotropic character of the linear compressibilities can be found after close inspection of the ambient pressure structure. Tl$_3$PSe$_4$ contains strong Tl-Se interactions within layers, i.e., predominantly along the a and c directions. In comparison, interaction distances between layers are uniformly longer, with increases approaching 6%. Between layers the Se(3)–Se nearest-neighbor distances are quite long (>4.1 Å) and, therefore, Se(3)–Se electrostatic repulsions generated by compression along the b axis should be relatively weak. Moreover, distance of closest approach of any atom directly along the b axis involves Tl(1)–Tl(2) at 3.8 Å. Given the large interatomic separations between layers and lack of potential electrostatic repulsions generated by compression directly along the b axis, one would predict an increase in $K_b$ over compressibilities in the a and c directions.

Although a mode-softening transition in Tl$_3$PSe$_4$ has been observed above 14 kbar, no structural transition involving a change in space group has been observed in these measurements. Owing to our uncertainty of ±1 kbar, it is unclear whether failure to detect a structural transition is due to insufficient pressure, since the transition is reversible, or whether the transition is of sufficient subtlety so as to preclude detection in this pressure range altogether. Higher pressures are attainable with this technique. However, Fluorinert 77 freezes if the pressure greatly exceeds 15 kbar. In order to attain higher pressures it will be necessary to change pressurizing fluids to a deuterated alcohol mixture. Further analysis of the data, i.e., full structure refinement, is in progress and this may yet lead to information about the mode-softening transition.

Complete three-dimensional high-pressure structure refinements using TOF (powder) diffraction data are not new (Brugger, Bennion & Worlton, 1967), but few, if any, high-pressure single-crystal neutron structure refinements have been performed using TOF techniques. While this technique offers important advantages by covering large areas of reciprocal space in a single pressure loading, not all regions of reciprocal space are accessible with one crystal orientation. A possible solution to this problem is to put two crystals with different orientations into the pressure cell, one above the other. Owing to the three-dimensional character of the data, software can be used to resolve independent orientation matrices for each crystal. Such an experiment has been performed at ambient pressure (no pressure cell) using four ruby spheres glued together in random orientations. Orientation matrices were obtained for each individual crystal, demonstrating the potential for multiple crystal work (Larson & Vergamini, private communication).

Conclusions

To our knowledge, this study presents the first single-crystal high-pressure experiment to be performed with TOF diffraction techniques. Pressures up to 20 kbar are accessible and the fixed crystal geometry allows the incident neutron beam to be brought in axially to the pressure cell, eliminating detection of Bragg scattering from the pressure-cell walls. Preliminary investigations on Tl$_3$PSe$_4$ show no difficulties in resolving peak positions and least-squares refined lattice parameters yield linear compressibilities where $K_a \approx K_c$ with $K_b$ being significantly larger. Ambient-pressure structural information is available that can account for the anisotropic character of these linear compressibilities. No structural phase transition has been observed at 15 kbar, although pressure calibration is
sufficiently coarse to prevent any definitive statement on this matter. Other experimental techniques are being pursued that will enhance pressure calibration as well as potential coverage of reciprocal space.

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References
