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Structure of NH_3-III at 1·28 GPa and Room Temperature

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Abstract. A simplified analytic analysis of the X-ray absorption and screening by a Merrill–Bassett diamond-anvil cell has been applied to intensity data from solid NH_3 at 1·28 GPa and room temperature. Phase III of solid NH_3 at this pressure has the $Fm3m$ space group with $a = 4{\cdot}968\,(3)$ Å and $Z = 4$ ($R = 0{\cdot}029$, 11 unique structure factors). The N atoms are at the 4(a) special position. The H atoms are probably disordered and could not be located.

Introduction. Since the introduction of the miniature diamond-anvil cell by Merrill & Bassett (1974), who improved on the design of Weir, Piermarini & Block (1969) (Fig. 1), there has been considerable interest in high-pressure structural studies of solids (Merrill & Bassett, 1975; Hazen & Burnham, 1974, 1975; Hazen, 1976*a*, *b*; Block & Piermarini, 1976). Recently this has been extended to the study of condensed gases; Hazen, Mao, Finger & Bell (1980) have examined CH_4 and Cromer, Mills, Schiferl & Schwalbe (1980) have examined N_2 at high pressure in this type of cell. The compressibilities of the noble gases Ne and Ar have been extensively studied by Finger, Hazen, Zou, Mao & Bell (1981) using one of these cells. Many of these workers have recognized that there are considerable absorption and shadowing effects by the cell and have attempted both analytic (Santoro, Weir, Block & Piermarini, 1968; Hazen, 1976*a*) and empirical (Hazen, 1976*a*; Finger & King, 1978; Denner, Schulz & d'Amour, 1978) methods to correct for these effects. Other workers have simply ignored these effects and have used the uncorrected intensities (Hazen *et al.*, 1980; Cromer *et al.*, 1980). For the case of a condensed gas, in which the single crystal fills the entire sample volume, the generalized analytic technique of Santoro *et al.* is the most complete; it allows for absorption by the anvils, gasket and sample with the cell held in any position relative to the incident and diffracted X-ray beams. We have effected a considerable simplification of this technique by assuming that the sample (NH_3) is non-absorbing, the gasket is a perfect absorber, and by collecting the data using the fixed φ mode (Finger & King, 1978).

The structures of the solid phases of NH_3 have aroused much interest recently. The low-temperature (2–180 K), ambient-pressure phase, solid I, has been investigated by X-ray single-crystal (Olovsson & Templeton, 1959) and neutron (Reed & Harris, 1961; Hewat & Riekel, 1979) powder diffraction techniques, and it was found to be primitive cubic, $P2_13$, with $a = 5{\cdot}073$ Å and $Z = 4$ at 77 K. More recently, in an optical study of NH_3 near room temperature (260–300 K) and high pressure (< 5 GPa), Hanson & Jordan (1980) found an optically isotropic phase, solid III, from 1 GPa to ~3·5 GPa and an optically anisotropic phase, solid IV, above ~3·5 GPa. Additionally, a hexagonal phase, solid II, was found at low temperature (~240 K) and high pressure (~0·5 GPa) and investigated by neutron diffraction (Eckert, Mills & Satija, 1983). In this study we report the structure of the room-temperature and 1·28 GPa phase III and the application of our simplified diamond-cell correction method to these data.

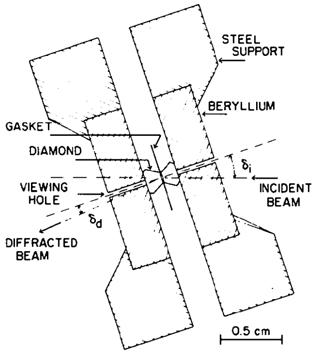

Fig. 1. A cross-section of the Merrill–Bassett diamond-anvil cell.

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Absorption and screening calculations

Transmission experiment. As can be seen in Fig. 1 the X-ray beam in a transmission experiment must pass through two thicknesses each of Be and diamond (D). Using the measured dimensions of these pieces for our cell and their respective absorption coefficients ($t_{\mathrm{Be}} = 0{\cdot}318$, $t_{\mathrm{D}} = 0{\cdot}134$ cm each and $\mu_{\mathrm{Be}} = 0{\cdot}4534$, $\mu_{\mathrm{D}} = 1{\cdot}877\ \mathrm{cm}^{-1}$ for Mo $K\alpha$ radiation) (*International Tables for X-ray Crystallography,* 1974), the attenuation of the transmitted beam by these components is

$$A = \exp(-0{\cdot}791/\cos\delta_i), \tag{1}$$

where δ_i is the angle between the X-ray beam and the normal to the cell.

The transmitted beam is further attenuated by the gasket aperture which is also a function of angle. We assume that the gasket is a perfect absorber of X-rays (the transmission coefficient for 0·1 mm Inconel foil is ~ 1% for Mo $K\alpha$ radiation) and that the sample volume is a right circular cylinder. The attenuation by the cell at some angle, δ_i, is given by

$$A' = \frac{2}{\pi}\,[a\cos\delta_i - (xT\sin\delta_i)/D^2], \tag{2}$$

where

$$x = (D^2 - T^2\tan^2\delta_i)^{1/2} \tag{3}$$

and, in radians,

$$a = \sin^{-1}(x/D). \tag{4}$$

The diameter of the sample volume is D and the gasket thickness is T. Equations (2)–(4) give the area of intersection for two ellipses which are the projections of the front and back of the sample volume along the X-ray beam. The intensities from the transmission experiments (see below) were fitted by least squares to the function

$$I = I_0AA', \tag{5}$$

where I_0 and T were refinable parameters; D(=0·15 mm) was measured optically. This fit and the contributing attenuations are shown in Fig. 2. The two lowest angle points were not used in the calculations, because at small angles the X-ray beam passes partially through the viewing holes in the Be supports. Inspection of the various contributions shows that most of the angular dependence is from the closing of the viewable aperture and not from absorption by the Be supports or the diamonds. Clearly the suggested construction of these cells using hemispherical pieces of Be (Keller & Holzapfel, 1977) is unnecessary and may lead to a high background from Be powder diffraction. The thickness, $T = 0{\cdot}100\,(3)$ mm, obtained from this fit was used to calculate the attenuation corrections for the diffracted intensities as described in the next section.

Diffraction experiment. For a diffraction experiment both the incident and the diffracted beams are attenuated by passing through Be and diamond at their appropriate angles of incidence, δ_i and δ_d. Using the measured dimensions of these pieces as noted earlier, the attenuation factor is

$$A = \exp\,[-0{\cdot}791\,(\cos\delta_i + \cos\delta_d)/\cos\delta_i\cos\delta_d]. \tag{6}$$

For the fixed φ mode (= 0°) on a Syntex $P\bar{1}$ diffractometer $\delta_i = \omega$ and $\delta_d = 2\theta - \omega$.

Inspection of Fig. 3 shows that the scattered intensity is further modified because the simultaneously illuminated and viewed fraction of the right circular cylinder sample volume is also a function of the angles of incidence, δ_i and δ_d. The edges of this active volume are assumed to be sharp because the gasket is a perfect X-ray absorber. Although the shape of this active volume is difficult to describe analytically, any cross section normal to the sample thickness is the intersection of three circles of equal diameter. They are the sample cross section and the projections of the front and back circular faces along the incident and diffracted beams; both projections are made to the active-volume cross-section location. The active volume can be calculated numerically by summing these areas for a series of steps along the cylinder axis. The centers of these circles are confined to be on a straight line by the fixed φ (=0°) geometry used in the data collection. Thus the area of intersection for the three circles is

$$C_j = \frac{D^2}{4}\,(2\beta_j - \sin 2\beta_j), \tag{7}$$

where, in radians,

$$\beta_j = \cos^{-1}(d_j/D) \tag{8}$$

and D is the sample diameter. The value of d_j is the distance between the outer two of the three circles, and depends on the relationship between the incident and diffracted beams at the cross-section position, t_j, in the sample volume. Thus, d_j is the maximum value of three possibilities

$$d_j = t_j\,|\tan\delta_i|, \tag{9a}$$

$$d_j = (T - t_j)\,|\tan\delta_d| \tag{9b}$$

or

$$d_j = |\,(T - t_j)\tan(\delta_d) - t_j\tan(\delta_i)\,|. \tag{9c}$$

The illuminated sample volume is computed numerically for a series of N steps, Δt, along the cylinder axis to give the attenuation factor

$$A' = \frac{4A}{\pi D2T}\sum_{j=1}^{N} C_j\Delta t. \tag{10}$$

Using the dimensions of the cell obtained by direct measurement and analysis of the transmission data, the diffraction data were corrected by these methods. After correction, the average deviation between equivalent reflections and their average was 8·5%. This represents considerable improvement over the uncorrected data where equivalent reflection intensities differed by as much as a factor of two and the average deviation was 25·6%.

Experimental. *Sample preparation.* The pressure cell was of standard Merrill & Bassett (1974) design with two $\frac{1}{8}$ carat brilliant-cut diamonds with 0·7 mm culets supported by 0·125″ (3·18 mm) thick Be disks (Fig. 1). An Inconel X750 gasket was precompressed to 0·15 mm thickness and a 0·25 mm hole was drilled in it for the sample chamber. The cell was partially assembled and cooled to below the boiling point of NH_3 which was then condensed into the open sample area. A ruby chip was included in the sample volume to facilitate pressure measurements. The cell was then closed and warmed to room temperature.

Crystals of NH_3-III were produced by pressurizing the cell to above the freezing point (1·0 GPa) whereupon a polycrystalline mass of NH_3 crystals formed. While the sample was observed, the pressure was then carefully adjusted to encourage a single crystal to grow at the expense of the others. Once a single crystal was obtained, the pressure was increased to the desired value. We did not observe any recrystallization as the pressure was increased in contrast to what had been observed for CH_4 (Hazen *et al.*, 1980). In the particular experiment reported here the final pressure was 1·28 GPa which is just above the anomalous-compression region of NH_3-III reported by Pruzan, Liebenberg & Mills (1982). At this pressure the diameter of the sample chamber was 0·15 mm. It should be noted that the procedure appeared to work only if the gasket was sufficiently thick. As the pressure was manipulated in the effort to produce a single crystal, the gasket became progressively thinner. After a few pressure cycles it became much more difficult to produce a single crystal and instead we always obtained several crystals around the edge of the sample chamber.

X-ray diffraction analysis. The loaded Merrill–Bassett cell was carefully centered on the Syntex $P\bar{1}$ diffractometer using the techniques described by Hamilton (1974). The setting angles for 10 reflections (5 each of [111] and [200]) recorded with graphite-monochromated Mo $K\alpha$ radiation were used to give the refined lattice parameter $a = 4{\cdot}968$ (3) Å. Examination of all the reflection intensities accessible with the cell revealed extinctions consistent with the face-centered space groups $Fm3$ and $Fm3m$. Because the volume of this unit cell is similar to that of the low-temperature 0·1 MPa NH_3-I phase, the contents are taken to be the same ($Z = 4$). In addition to the crystal described in this work two other samples were examined at different pressures; we obtained the lattice parameters $a = 4{\cdot}920$ (3) Å at 1·58 GPa and $a = 4{\cdot}760$ (3) Å at 3·16 GPa. These results are in good agreement with the static compressibility studies of Pruzan *et al.* (1982) and the X-ray powder studies of Olinger & Mills (1983).

To assist in the computation of diamond-cell screening and absorption corrections, the transmission through the pressure cell was measured with the generator at reduced power (20 kV and ~2 mA) and at 5° intervals for $-45° < \varphi < 45°$ with $\chi = 0°$ and $\omega = 0°$. From these measurements it was noted that the pressure cell was rotated $-7{\cdot}5°$ from $\varphi = 0°$. Analysis of these data using equations (1)–(5) as described earlier indicated that at this pressure the gasket was 0·100 (3) mm thick.

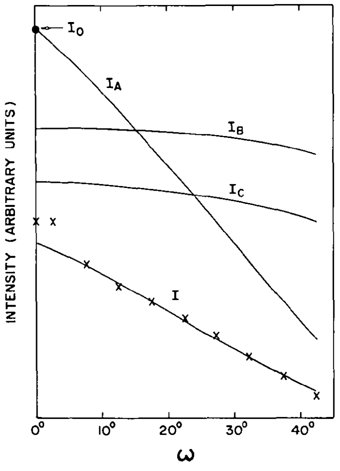

Fig. 2. Calculated transmitted intensity for various components of the Merrill–Bassett cell, as a function of the angle of incidence: I_o through gasket pinhole ($\delta_i = 0°$); I_A through gasket pinhole; I_B through both Be disks; I_C through both diamond anvils; $I = I_AI_BI_C$ through assembled cell; X, observed transmitted intensity.

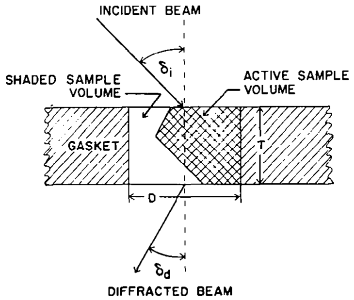

Fig. 3. Detailed view of the incident and diffracted X-ray beams near the sample volume. The cross-hatched region is the active sample volume.

All reflections for the primitive cell accessible within the limits imposed by the pressure cell ($2\theta < 45°$) were collected in the fixed φ ($= -10°$) mode (Finger & King, 1978) using θ–2θ scans of $1°\ \mathrm{min}^{-1}$ over $\pm 1°$ from the $K\alpha_1$–$K\alpha_2$ doublet. A background count for 0·5 of the scan time was taken at each end. Three reflections monitored periodically during the data collection showed no significant change in intensity. Of the 408 reflections examined only 76 were allowed by the space group and not blocked by the pressure cell. Their intensities were corrected for Lorentz and polarization effects (Azaroff, 1955) and for screening and absorption by the pressure cell by equations (6)–(10). The range of transmission factors was 0·174–0·416.* Equivalent reflections in *Fm*3*m* were then averaged to give 11 unique structure factors (Table 1) and weights ($= 1/\sigma_F^2$) were assigned from the estimated standard deviations in these averages. Examination of the corrected intensities did not reveal any inequalities consistent with the lower-symmetry space group (*Fm*3); therefore *Fm*3*m* was chosen. The four N atoms were assigned to the 4(*a*) special position which has *m*3*m* point symmetry. Assuming that the NH_3 molecules maintain their normal geometry, the 12 H atoms in this structure are disordered over as many as 192 positions; therefore they were left out of the structure. A refinement of the two parameters (scale factor and N temperature factor) yielded the residuals $R = 0{\cdot}029$ and $R_w = 0{\cdot}027$ and the calculated structure factors in Table 1. The N temperature factor thus obtained was $U = 0{\cdot}083\ (4)\ \text{Å}^2$. The highest peak in a difference Fourier synthesis was $0{\cdot}03\ \mathrm{e}\ \text{Å}^{-3}$ and could not give any indication of the highly disordered H-atom positions.

Discussion. The structure of NH_3-III is closely related to the low-temperature 0·1 MPa NH_3-I phase. Both have essentially the same unit-cell volume and contents. Moreover, the N-atom positions in phase I nearly form the face-centered array that is found in phase III. In the standard descriptions the unit cell of phase I is shifted $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$ from that for phase III. The H atoms in phase I are in ordered positions so that each NH_3 forms hydrogen bonds to six other molecules, three as H-atom acceptors and three as H-atom donors. These six NH_3 molecules are the nearest neighbors (3·35 Å), and in this nearly f.c.c. array there are six more NH_3 molecules which are slightly farther away (3·88 Å). In phase III at 1·28 GPa the N atoms form an exact f.c.c. array in which each NH_3 has 12 nearest neighbors all at 3·513 (2) Å which is only closer by 0·10 Å than the average distance for the 12 neighbors in phase I.

Table 1. *Observed and calculated structure factors for* NH_3-III

H	K	L	F_o	F_c	σ_F
1	1	1	268·8	275·6	21·2
0	0	2	242·3	235·1	19·8
0	2	2	136·4	134·5	14·2
2	2	2	81·1	84·0	12·1
1	1	3	94·7	93·9	12·4
1	3	3	38·7	41·5	10·9
3	3	3	21·5	21·0	11·1
0	0	4	54·3	55·6	11·6
0	2	4	32·8	38·1	10·7
2	2	4	21·1	26·9	11·2
1	1	5	17·1	21·0	11·1

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* A table of the individual raw and corrected intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39489 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.