Structure of Deuterated Ammonia IV

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The structure of the high-pressure phase IV of ammonia has been solved from neutron powder diffraction data from ND_3, and preliminary studies have been made of the structural pressure dependence to 9 GPa. The structure is orthorhombic, not hexagonal close packed (hcp) as previously thought. The nitrogen atoms have a pseudo-hcp arrangement, but the deuterium atoms do not and are ordered at all pressures studied. The internal molecular geometry is not significantly distorted from that found in phase I at ambient pressure, but the hydrogen bond geometry is more distorted and is unexpectedly complex.

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There has been a long-standing and wide interest in the high-pressure behavior of simple hydrogenous molecular "ices" such as H_2O, NH_3, and CH_4 which has aimed at obtaining fundamental information such as the changes in the interatomic potentials with interatomic separation. Extensive studies of ice itself have explored the changes in the hydrogen bonding with pressure and have searched for the transition to symmetric ice where the hydrogen bond becomes centered [1]. Ammonia is an important member of this group of ices. It has weaker hydrogen bonding than H_2O and has a "shared" hydrogen-bond geometry with three hydrogen atoms bonding to a single lone pair [2]. This has led to a fundamental interest in understanding how these differences affect the high-pressure behavior. Also, ammonia is a major constituent of the Jovian planets and a knowledge of its high-pressure properties is important for planetary modeling [3].

Accurate structural information is an essential basis for a full understanding of high-pressure behavior, but in the case of ammonia accurate structural studies have been confined to modest pressures. The phase diagram (see Fig. 1) shows that three solid phases are known at low pressures, with structures that are either close packed (phase II, Ref. [4], and phase III, Ref. [5]) or pseudo close packed (phase I, Refs. [6,7]). In the low-temperature phase I the molecules are ordered [6,7], while at higher temperatures in phases II and III the molecules are rotationally disordered [4,5]. At higher pressures, phase IV is found over the entire temperature range studied to date [8,9] and is the first phase of ammonia to be found stable over an extended range of pressure [10]. Knowledge of the structure and structural pressure dependence of phase IV is thus important for understanding the high-pressure properties of ammonia up to and beyond molecular dissociation. However, existing information on the structure of phase IV is limited and uncertain.

Unpublished x-ray work by Mills and Olinger [9] found phase IV to have space group $P6_3/mmc$, with two molecules per unit cell and a hexagonal-close-packed (hcp) structure. In contrast, Raman studies by Gauthier *et al.* [10] found that four molecules per unit cell are required to account for the number of observed modes, based on an assumption that the space group is $P6_3/mmc$. Such an arrangement can be ruled out on density grounds, but—though not explicitly stated—this study apparently shows that the hcp structure proposed by Mills and Olinger [9] is inconsistent with optical data. However, subsequent further x-ray work confirmed the view that the structure of phase IV *is* hcp [11]. This structure implies a high level of orientational disorder.

There is a clear need for a definitive determination of the structure of phase IV, including the location of the hydrogen atoms and the nature of their ordering. This requires neutron diffraction techniques. Until recently, detailed neutron diffraction studies have been limited to pressures below 3 GPa, but the recent development of the Paris-Edinburgh pressure cell has now extended the pressure range for neutron diffraction to more than 10 GPa [12]. This facility has made it possible to obtain

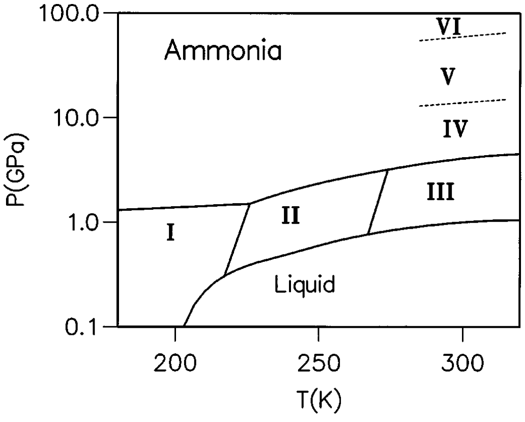

FIG. 1. The phase diagram of ammonia after Ref. [10].

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high quality neutron diffraction patterns from ammonia phase IV, and we have now solved its crystal structure.

The Paris-Edinburgh cell and its use for accurate high-pressure structural studies using time-of-flight neutron diffraction techniques at the UK pulsed neutron source ISIS are described in detail elsewhere [12,13]. The special modifications and procedures required to load gases like ammonia into the cell have been recently described in Ref. [14]. Patterns from such samples contain some diffraction peaks from the anvils (tungsten carbide in this case), because the full shielding required to remove all nonsample scattering is not compatible with the present gas-loading procedures. However, for a strongly scattering sample like ammonia, the residual contaminant scattering can be kept at a relatively low level—as shown in Fig. 2 below. Patterns collected from early loadings of ammonia also showed strong texture effects, which are a common problem in samples produced by solidification of liquids and gases, but pressure and temperature cycling [14] produced a sample of ND_3 (Ref. [15]) that was largely free from such texture effects [16]. Patterns were collected from this sample at pressures of 4.5, 5.0, 7.0, and 9.5 GPa, as determined from the x-ray equation of state [11] using the procedure described by Klotz *et al.* [14]. (The initial sample volume of ~80 mm^3, loaded at ~6 bars and 250 K, was reduced by a factor of about 2 at the top pressure of 9.5 GPa.) As we have described in detail in Ref. [14], numerous, strong, non-hcp peaks were easily visible that are better fitted by an orthorhombic unit cell: Clearly ND_3-IV does *not* have a hexagonal close-packed structure [13,14]. The full structure of phase IV has now been solved using the 5.0 GPa data (shown in Fig. 2), which were collected for a longer time than at the other three pressures. The refined unit cell dimensions at 5.0 GPa are $a = 3.2495(4)$, $b = 5.6576(6)$, and $c = 5.3556(5)$ Å [17]. These values are close to, but clearly differ from, the relationships required by a hexagonal lattice ($b = \sqrt{3}a$) and an ideal hcp structure ($c = \sqrt{8}a/\sqrt{3}$).

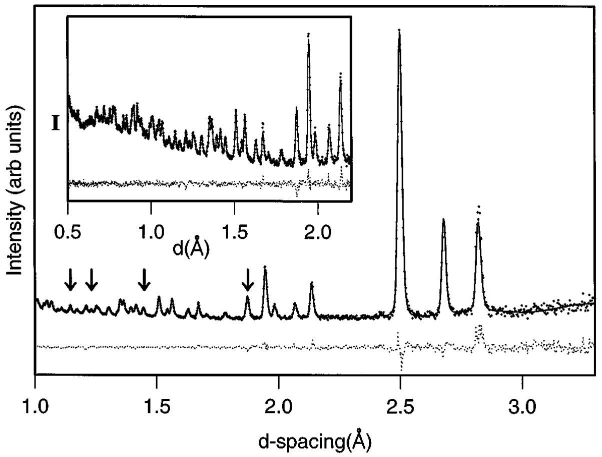

FIG. 2. Rietveld profile refinement fit to a diffraction pattern collected from ND_3 phase IV at 5.0 GPa. The difference between the observed and calculated profiles is shown below the diffraction pattern as a dotted line. The arrows mark the first four significant reflections from the tungsten carbide anvils. The inset shows the short *d*-spacing range enlarged.

As a basis for solution of the structure, the nitrogen atoms were assumed to have the pseudo-hcp arrangement indicated by the x-ray data [9]. As already shown [14], five space groups are consistent with the observed reflections and a pseudo-hcp nitrogen arrangement, and, of these five, $P2_12_12_1$ is the most likely on the basis of the apparent systematic absence conditions. So this symmetry was adopted for the initial search, with the internal molecular geometry taken to be as found at ambient pressure in the (ordered) phase I (Ref. [7]). The unit cell contains four molecules [14], all related in position and orientation by the space-group symmetry, and the structure was assumed to be ordered (see below). The orientation of the molecules was varied through 20° on each of the three Euler angles in turn, over all possible configurations, using the rigid body option in the GSAS structure refinement package [18]. At each step, the scale factor and an overall thermal parameter were least-squares (Rietveld) refined to obtain a measure of the fit, expressed as χ^2. The search produced several minima in χ^2 with an angular half-width of ~30°. The deepest minima all had χ^2 values of ~5, and were found to be related by either the space group symmetry or the 3-fold symmetry of the molecule. All the other minima had χ^2 values of 11 or more. At each of the $\chi^2 \sim 5$ minima the Euler angles were refined and χ^2 dropped to ~4. The same procedure was then applied to the other four possible spacegroups, and no χ^2 values below 7–8 were found—even after allowing the Euler angles to vary around the minima in the 20°-step search. It thus appears that the configuration giving the $\chi^2 \sim 5$ minima in $P2_12_12_1$ is a unique solution, and this solution also gives a plausible molecular arrangement with reasonable bond lengths and angles.

This configuration was used for full refinement of the data. All atoms are in general positions in $P2_12_12_1$, and so there are twelve atomic fractional coordinates to vary, along with two isotropic thermal parameters (one each for nitrogen and deuterium), the scale factor, lattice parameters, and peak width parameters. The contaminant scattering from the tungsten carbide anvils was also included in the calculated profile; the lattice parameters, the phase fraction, an overall thermal parameter, and peak width parameters for tungsten carbide were refined together with the variables for ammonia, using a two-phase Rietveld procedure [18]. A preferred orientation model with an $0k0$ axis was found to give a significantly improved fit to the ammonia profile and was adopted. The refined value of the preferred orientation parameter showed the sample to be significantly non-randomly oriented, but no strongly so; the incorporation of the effect in the refinement did not alter any relative atomic position by more than 0.04 Å. The final best fit is shown in Fig. 2. It is clearly very good, and gives a χ^2

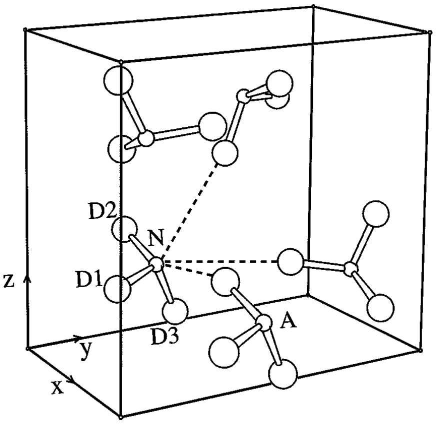

FIG. 3. The structure and unit cell of ND_3 phase IV. The dashed lines denote the short D...N hydrogen bonds. The molecule labeled *A* lies in the adjacent unit cell along *x*.

value of 2.09. The refined atomic coordinates at 5.0 GPa are $(x = 0.2604(11), y = 0.3509(4), z = 0.2563(5))$ for the N atom, $(0.3796(16), 0.1918(9), 0.2352(11))$ for D1, $(-0.0294(23), 0.3340(9), 0.3240(12))$ for D2, and $(0.2312(24), 0.4238(7), 0.0902(12))$ for D3.

The ammonia molecule is not constrained to have 3-fold symmetry by the space group, but the final refinement of the 5.0 GPa data produced values for the three intramolecular N-D bond lengths that are of a similar magnitude [0.987(5) Å, 1.014(6) Å, and 0.985(7) Å] with similar D-N-D angles [108.7(5)°, 108.5(5)°, and 105.9(7)°]. A refinement with the three N-D bond lengths constrained to be equal and the three D-N-D angles all fixed at 107.8° (the value found in phase I, Ref. [7]) did not give a significantly poorer fit. Thus—with the present data—there is no significant evidence of distortion of the 3-fold molecular symmetry in phase IV. Tests were also made to look for evidence of partial orientational disorder of the molecules just above the transition, at 4.5 and 5.0 GPa, by starting refinements with the D atoms disordered over the 12 sites ~1 Å from each N atom towards its 12 neighboring N atoms. The refined site occupancies agreed with Fourier difference maps in showing the structure to be at least 90% ordered at both these pressures, and there is no significant evidence against full ordering. This appears contrary to the suggestion of Gauthier *et al.* [10] that the observation of new lattice modes only above 5–6 GPa indicates progressive orientational ordering in the range 3.5–6 GPa.

The structure is shown in Fig. 3. Consistent with x-ray results [9,11], the nitrogen atoms lie within 0.11 Å of the relative positions of an hcp arrangement. In this respect, phase IV is most similar to phase II—the rotationally disordered hcp phase [4]. However, phase IV is more akin to phase I in having fully (or nearly fully) ordered D sites at all pressures measured and a similar H-bonded network. As is found on cooling, compression of ammonia results in transformations directly from rotationally disordered structures (phases II and III) to a fully ordered structure.

A comparison of the structures of phase IV and phase I (Refs. [6] and [7]) is shown in Fig. 4. Both structures have a pseudo-close-packed molecular arrangement, pseudo-fcc in the case of phase I and pseudo-hcp in the case of phase IV. However, the displacements from the ideal close-packed arrangement of nitrogen atoms are about twice as large in phase I as in phase IV. Pseudo-close-packed layers can be seen labeled *A*, *B*, and *C* in phase I and *A*, *B*, and *A*′ in phase IV. (The symmetry of phase I is more evident if the layers are taken perpendicular to a [111] direction, as outlined by the dotted lines. But the description in terms of the *A*, *B*, and *C* layers gives the closest correspondence with the phase IV structure.) Ammonia has an unusual shared H-bond geometry, with three H atoms and a lone pair that is a receptor for H bonds from three neighboring atoms [2]. This can be seen in both structures. As shown, the labeled N atoms in phase I has N-D...N and N...D-N bonds to three neighboring atoms

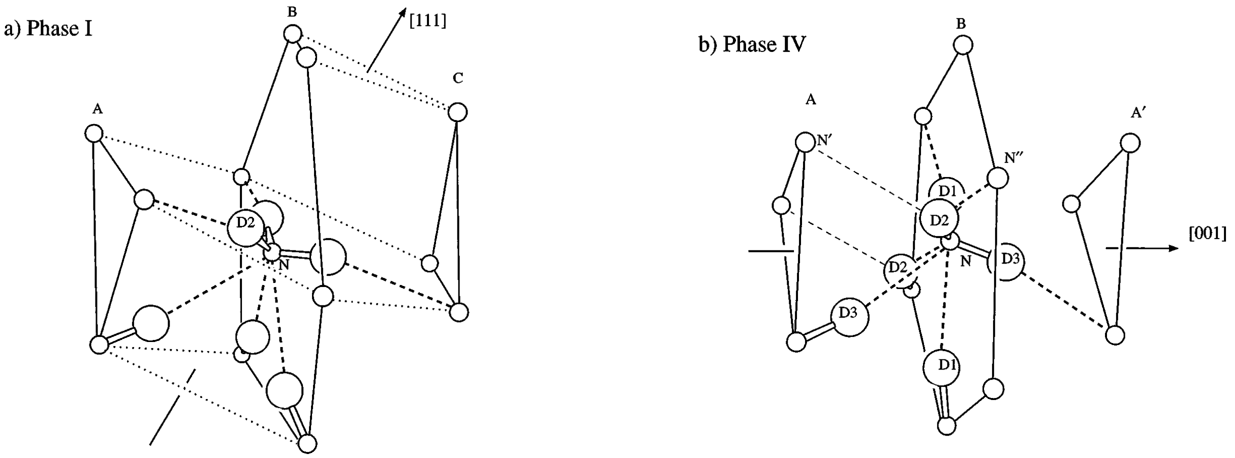

FIG. 4. The nearest-neighbor coordination shells of ND_3 in (a) phase I (after Ref. [7]) and (b) phase IV. The pseudo-close-packed layers are outlined by continuous lines and are labeled *A*, *B*, and *C* in phase I and *A*, *B*, and *A*′ in phase IV. The dotted lines in (a) outline the pseudo-close-packed layers normal to the [111] direction as explained in the text. The thick dashed lines denote the short D...N hydrogen bonds in both structures, and the thin dashed lines in (b) show the D...N contact of the bifurcated hydrogen bond discussed in the text.

in the B layer, two in the A layer, and one in the C layer. The bonding in phase IV is similar except that the bond through D2 is to N'' in the B layer, though an additional, longer bonded contact to N' in the A layer remains (as shown by the light dashed lines and discussed below). And layer A in phase IV is related to layer A in phase I by a 60° rotation around the pseudo-3-fold axis along [001].

Phase I has a $6 + 6$ coordination, with the six hydrogen-bonded N-N distances at 3.38 Å, significantly shorter than the non-hydrogen-bonded N-N contacts at 3.94 Å. The corresponding neighbors in phase IV are in six pairs each with a different N-N distance ranging from 3.17 to 3.39 Å, and four of these distances lie in the small range between 3.20 and 3.30 Å. Thus the difference between the bonded and nonbonded N-N contacts in phase IV is much less pronounced than it is in phase I. Also, the intermolecular hydrogen-bond geometry of phase IV is quite distorted from that found in phase I. Two of the N-D...N angles are similar to those found in phase I, but the bond involving D2 ($N\text{-}D2\ldots N''$) is more bent at 149° instead of 160°. The D...N distance of 2.34 Å for this hydrogen bond is also the longest among the three clearly identifiable hydrogen bonds. As already noted, D2 also has a second D...N contact of 2.57 Å to a nitrogen atom N' in the A layer with an angle ($N\ldots D2\text{-}N'$) of 127°. This D...N distance is shorter by 0.26 Å than all the other unbonded D...N contacts and, unlike them, is shorter than the sum of the van der Waals radii for deuterium and nitrogen (2.75 Å). It thus appears that D2 differs in being hydrogen bonded to two ammonia molecules. Such bifurcated hydrogen bonds are known as an occasional feature of ammonium and amide groups [2]. Nonetheless it is perhaps surprising to find such bonds in a system as relatively simple as ammonia.

The changes in the phase IV structure with increasing pressure appear generally to increase the differences between the phase I and phase IV structures. The distortion of the molecular packing from an ideal pseudo-hcp arrangement is due partially to the axial ratios differing from the ideal values ($b = \sqrt{3}a$ and $c = 1.633a$) but is mainly due to the molecular centers not being located on pseudo-hcp sites within the unit cell. The axial ratios show no significant change with pressure—contrary to Mills and Olinger's data [9], which show c/a decreasing to reach the ideal value at ~6 GPa. However, the nitrogen positions show a clear trend to move towards ideal hcp positions with increasing pressure and the distance from the ideal hcp position reduces by nearly 30% between 5 and 9 GPa.

The structure of phase IV, as now revealed, gives a quite new perspective on the nature of the eventual bond centering expected at higher pressure. The transitions at ~12 GPa to phase V and at ~60 GPa to phase VI were proposed on the basis of the observed Raman modes to produce cubic structures [10], and possible structures with centered hydrogen bonds were suggested for phase VI [10]—one with a primitive cubic and another with an fcc nitrogen arrangement. However, x-ray results [11] have since indicated that the hcp-like nitrogen arrangement of phase IV persists up to at least 56 GPa. It would require a large structural rearrangement to transform from a phase-IV-like configuration to that of the cubic structures, and the path to molecular dissociation and bond centering in ammonia is likely to prove much more complex than previously thought [10].

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