Ammonia Monohydrate VI: A Hydrogen-Bonded Molecular Alloy

J. S. Loveday and R. J. Nelmes
Department of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom

(Received 30 June 1999)

The detailed crystal structure of ammonia monohydrate phase VI—stable above 6.5 GPa at 300 K—has been determined from neutron diffraction data. It has a body-centered cubic arrangement of molecular centers that are randomly occupied by water or ammonia molecules. The hydrogen-atom positions suggest that the structure is hydrogen bonded and the phase thus appears to be an H-bonded molecular alloy. This type of structure may accommodate nonstoichiometry and be stable to very high pressures.

PACS numbers: 62.50.+p, 61.12.Ld

It has long been known that water mixes with a wide variety of species (for example, methane, xenon, acetone) to form inclusion compounds [1], the clathrate hydrates, which have closely related structures based on cages [1]. However, there are a number of other water-based mixtures whose structures are very different. The ammonia di-, mono-, and hemihydrates differ from the clathrate hydrates in that both ammonia and water are involved in H bonding [2]—in the clathrate hydrates H bonding is confined to the water molecules [1]—and they are the simplest systems to contain mixed O-H$\cdots$N and N-H$\cdots$O hydrogen bonds. Such H bonds linking O to N are common and are important to the function of biological molecules [3]. In addition, the outer planets Uranus and Neptune [4] and the satellites Triton and Titan [5] are believed to be largely composed of ice and ammonia. A recent theme in *ab initio* modeling studies has been the calculation of the properties of likely planetary components such as methane, ice, and ammonia under planetary conditions [6]. Mixing is likely to occur in planetary environments and so the ammonia hydrates are more realistic planetary "minerals" than are the pure systems modeled until now.

The clathrate and ammonia hydrates are stable at or close to ambient pressure. High pressure can stabilize other types of mixture structure, such as $H_2O \cdot H_2$ [7], which has a structure related to that of ice VII. Ice VII has two interpenetrating ice I_c-like H-bonded networks of water molecules [8] arranged so that the molecular centers form a pseudo-body-centered cubic (bcc) arrangement. $H_2O \cdot H_2$ has only one of the ice I_c-like networks with the H_2 molecules believed to occupy the sites of the water molecules of the second network [7].

All mixture structures determined so far have clearly defined sites for molecules of water and the second component, with no evidence of substitutional disorder. And $H_2O \cdot H_2$ remains the only example of an ice-VII-related structure reported until now in a water mixture. In this paper we report the structure of a new phase of ammonia monohydrate (AMH) which is both substitutionally disordered and ice-VII related.

Samples of deuterated [9] ammonia monohydrate liquid were prepared by condensing the required amount of ND_3 onto a preweighed amount of D_2O ice at 77 K in a sealed system. The mixture was warmed to room temperature, shaken to ensure mixing and then cooled to 220 K where the liquid is stable at ambient pressure. The sealed system was opened and some of the liquid was frozen into the tungsten carbide anvils of a Paris-Edinburgh neutron-diffraction pressure cell [10] held at 77 K. This anvil assembly was transferred (at 77 K) to the pressure cell and a load of five tonnes applied to seal the system which was then warmed to room temperature prior to transfer to the PEARL beam line of the ISIS pulsed neutron facility. In all samples studied, the cell and sample were first cooled to 170 K at this load, which produces a pressure of less than 0.5 GPa, and diffraction patterns were collected at this low pressure to verify that the sample was stoichiometric single-phase AMH phase I. The phase diagram of AMH is relatively complex with seven solid phases to 6 GPa (Fig. 1) [2]. Two pressure-temperature paths were followed to phase VI as shown in Fig. 1. One involved compression at 170 K through phase II and phase IV to 6.5 GPa, and warming through the transition to phase VI at ~270 K. The second path involved warming from phase II to phase III at 1.2 GPa and 220 K, compression to 6.5 GPa (where the sample remained in phase III), and warming to phase VI at 270 K. For each path, at least two separate loadings were used, one with and one without a lead pressure calibrant.

In contrast to the other phases of AMH [2], the diffraction pattern of AMH VI (Fig. 2) is remarkably simple. It is dominated by a single peak with only four other discernible peaks. All the peaks can be indexed with a cubic unit cell ($a = 3.37$ Å) whose systematic absences are consistent with a body-centered lattice. The dimensions of the unit cell are remarkably similar to those of ice VII at this pressure [11] and Patterson (pair correlation) maps using space group $Pm\overline{3}$ (the lowest symmetry Patterson group for the cubic system) reveal peaks at 0.5, 0.5, 0.5, and 0.16, 0.16, 0.16. This is what would be expected for a bcc arrangement of molecular centers with the D sites ~1 Å

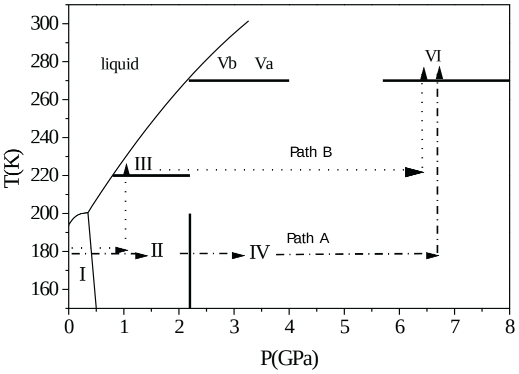

FIG. 1. The phase diagram of ammonia monohydrate [4]. The dotted and dot-dashed lines denote the two different routes followed to make phase VI.

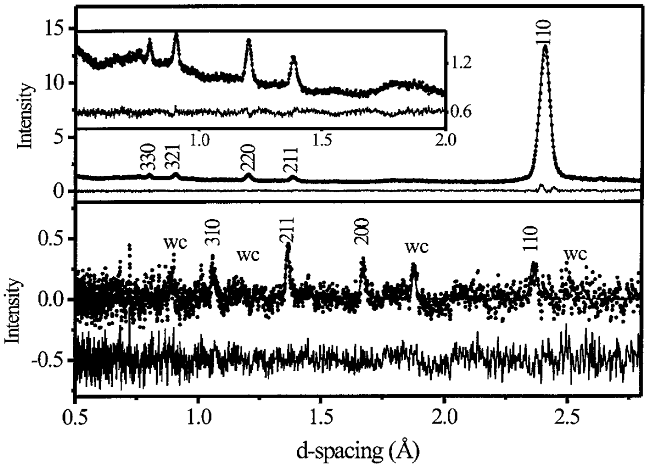

FIG. 2. Profile refinements of deuterated (upper plot) and hydrogenous AMH VI. The dots show the observed pattern and the solid lines the fit to these data. Below the fit is shown the difference between the observed and calculated patterns. Visible sample reflections in both patterns are labeled with their (hkl) indices. Contaminant reflections from the tungsten-carbide anvils in the lower plot are marked WC.

away along $\langle 111\rangle$ directions. This arrangement is also highly plausible since the shortest distance between centers is ~2.9 Å—a reasonable value for an H-bond distance.

The fact that no non-body-centered reflections can be observed rules out an ice-VII-like structure whose interpenetrating H-bonded networks break body-centering symmetry. Body centering also requires all molecular centers to be identical in the average structure and so implies substitutional disorder of water and ammonia molecules. There are two possible arrangements. The first, in space group $I\bar{4}3m$, has four equally occupied D sites per molecular center with O(N)-D bonds along $\langle 111\rangle$ directions which have a tetrahedral relationship (for example, [111], $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$). Body centering then requires that the D sites around all O(N) sites are in the same directions (unlike the structure of ice VII). The second arrangement, in space group $Im\bar{3}m$, has eight D sites per molecular center with the O(N)-D bonds along all eight $\langle 111\rangle$ directions. Both of these models were tested against the observed data by refinement. The model with four D sites gave a 30% poorer fit to the data (based on the reduced goodness of fit, χ^2 [12]) and gave negative thermal motion for the O(N) site. Accordingly, the model with eight sites (Fig. 3) was used for further refinement.

With eight D sites per molecular center, this model implies considerable disorder of the molecular orientations. To explore the detailed nature of the orientational disorder, a more general model with the O(N)-D bonds directed along the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions was refined. The occupancies of the D sites refined to show that ~80% of the N(O)-D bonds are directed along the $\langle 111\rangle$ directions with the remainder all along $\langle 110\rangle$.

This model was adopted for the final refinements shown in Fig. 2, which gave 3.2727(2) Å for a, the lattice parameter; 0.032(8) Å^2 for U_{iso} [O(N)], the mean O(N) thermal motion; 0.035(11) Å^2 for U_{iso} (D), the isotropic thermal motion of the D sites [13]; and 0.976(4) Å for the O(N)-D bond length, L, where the deuterium atoms were distributed over 16(f) (x, x, x) and 24(h) (x', x', 0) sites with $x = L/(\sqrt{3}\,a)$ and $x' = L/(\sqrt{2}\,a)$. The refined occupancies were 0.26(5) for the 16(f) sites and 0.039(14) for the 24(h) sites, giving 82(16)% along $\langle 111\rangle$ and 18(6)% along $\langle 110\rangle$, with a total occupancy of 5.1(9) D atoms in the average unit cell. Thus the refined O(N)-D bond length and thermal parameters are all reasonable, and the average D content freely refines to the correct value of five D atoms per unit cell. If the total occupancy is constrained to this value, the 16(f) and 24(h) site occupancies refine to 87(5)% and 13(5)%, respectively.

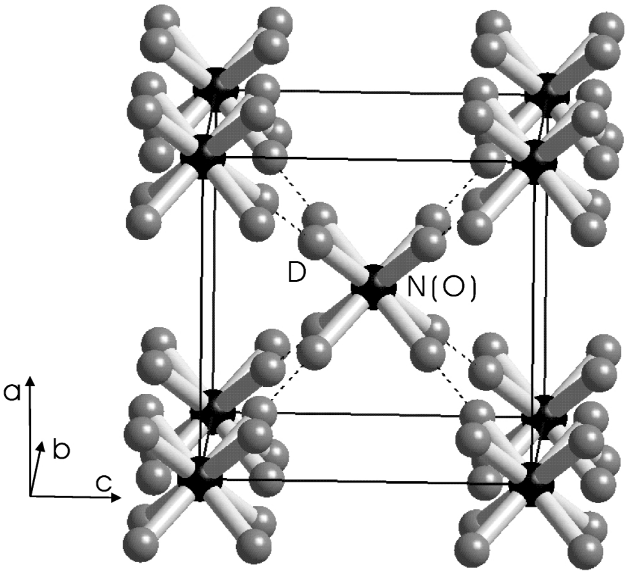

FIG. 3. The body-centered structure of AMH VI. For clarity, only D sites along $\langle 111\rangle$ directions are shown; the small D density found along $\langle 110\rangle$ directions (see text) has been omitted.

As a further check of the structure solution, a sample was produced using hydrogenous water and ammonia. Deuterium accounts for 60% of the total scattering in AMH and so hydrogenation—which halves the scattering amplitude of the H(D) site and changes the sign of its scattering—produces large changes in the pattern. Hydrogenation also gives rise to a very large incoherent background [9] and hence a relatively poor pattern—even in the ~24 h of this data collection. However, key features are clear (Fig. 2). For example, the 200 reflection is invisible in the deuterated pattern but is one of the strongest reflections in the hydrogenous one; and conversely the dominant 110 reflection of the deuterated pattern is strongly reduced in intensity. The fact that the same structure can account for both hydrogenous and deuterated patterns when they are so different provides further compelling evidence that the solution is correct.

The question then arises as to whether the structure is hydrogen bonded. The fact that the O(N)-D bonds are largely directed along ⟨111⟩ towards nearest-neighbor atoms would suggest that it is. The N(O)···N(O) distance is 2.921 Å, giving a D···N(O) distance of ~1.9 Å, which is comparable to the D···O distance in ice VII at this pressure [11] and thus implies strong H bonding. The bcc arrangement of molecular centers also supports the case for H bonding: it provides the densest packing consistent with tetrahedral coordination, which is the most favorable for H bonding. This contrasts with ammonia which appears to be relatively weakly H-bonded and whose structures all have a close-packed or pseudo-close-packed arrangement of molecular centers [14–16].

The fact that the O(N)-D bonds are directed along all eight ⟨111⟩ directions seems surprising given this evidence of H bonding. As has been stated, these directions can be divided into two groups of four each of which has a tetrahedral relationship—in Fig. 4, (i) the corner atoms labeled O, a, b, c around the central molecule and (ii) those labeled O', a', b', c'. An insight into how an eightfold distribution of D atoms may arise in what appears to be an H-bonded structure can be obtained from a consideration of the possible local arrangements around a given ammonia molecule. The diagrams in Fig. 4 show such a molecule with its eight nearest-neighbor molecules. These may be either ammonia or water—on average four of each—with two of the eight having O(N)-D bonds directed towards the central ammonia molecule (and thus five D atoms in the average unit cell). (It does not matter whether these are N-D or O-D bonds for the purposes of this argument, but the ambient pressure structures of the three ammonia hydrates suggest that O-D···N hydrogen bonds are much stronger than N-D···O [2], making it likely that the majority of N-D or O-D bonds directed towards ammonia molecules will in fact be O-D bonds.)

If one D atom, D1, is placed along the ⟨111⟩ leading from the site labeled O to the central molecule (Fig. 4) then there are three distinctly different ways the second D atom, D2, can be placed. Figure 4(a) shows one of these, with D2 placed on a direction which is a member of the same tetrahedral group—that is on the ⟨111⟩ directions leading from sites a, b, or c. In such an arrangement, it is not possible to direct the three N-D bonds of the central ammonia molecule along ⟨111⟩ directions of the same tetrahedral group without breaking the ice rules. The only possible arrangement which places the ammonia D atoms close to ⟨111⟩ is that shown in Fig. 4(a) where the N-D bonds are directed along ⟨111⟩ directions in the other tetrahedral group from that of the incoming O(N)-D bonds. Hence, the three D atoms of the ammonia prevent the formation of a single extended tetrahedral H-bonded network and rule out an ice-VII-like structure with separate interpenetrating networks. The arrangement shown in Fig. 4(a) has D···D distances of ~1.85 Å from D1 and D2 to the ammonia D atoms, which is shorter than the value of 2.05 Å expected for a minimum H···H distance [17]. However, it may be that the molecular centers are displaced from the average (0.5, 0.5, 0.5 and 0, 0, 0) positions such that the instantaneous H···H distances are greater than 1.85 Å. The O(N) thermal parameter is almost 3 times larger than that found in fully ordered ice VIII at a similar pressure and temperature [11]. If we assume that the true O(N) thermal motion in AMH VI is the same as that determined for oxygen in ice VIII (0.012 Å^2 at 5 GPa and 280 K [11]), then the additional contribution from multisite disorder (~0.019 Å^2) would suggest that the O(N) atoms are displaced ~0.25 Å from the average sites—an amount

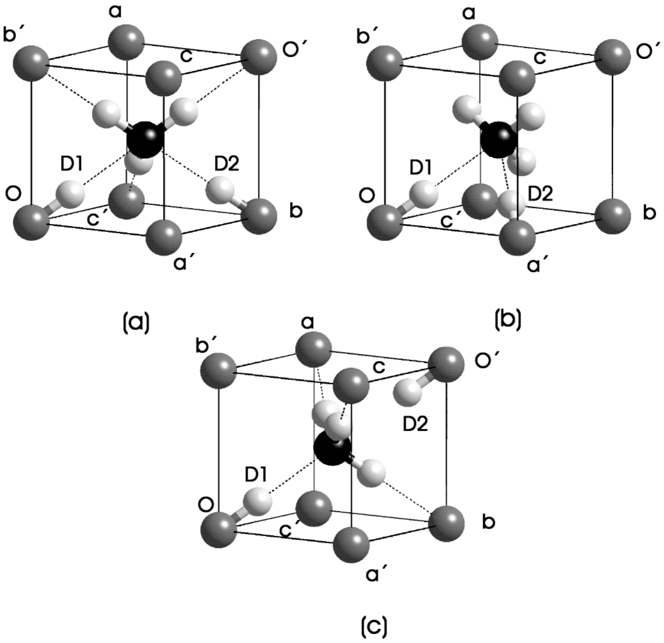

FIG. 4. The nearest neighbor environment of an ammonia molecule in AMH VI. The three diagrams show the three possible distinct ways of H bonding such a molecule to the surrounding eight O(N) atoms.

sufficient to relieve the short D···D contacts. However, even with this disorder, the D···D contacts lie close to the minimum distance of 2.05 Å [17] and the structure is quite densely packed.

Figure 4(b) shows the second possible arrangement, with D1 and D2 on $\langle 111\rangle$ directions which are in different tetrahedral groups. The ammonia molecule could be orientated so that its N-D bonds were directed along either group of $\langle 111\rangle$ directions, but the ammonia lone pair would then be directed towards either D1 or D2. We suggest a more plausible orientation is that shown. Here the molecule is rotated so that the ammonia lone pair bisects the H bonds donated by D1 and D2. As a result, the ammonia N-D bonds are directed close to $\langle 110\rangle$.

The final arrangement shown in Fig. 4(c) has D1 and D2 on oppositely directed $\langle 111\rangle$ directions in different tetrahedral groups. The only plausible orientation for the ammonia molecule is that shown with the O(N)-D2 bond opposed to three N-D bonds of the ammonia molecule. This gives rise to short D···D distances—which may again be relieved by multisite disorder of the O(N) sites. But, since the O(N)-D2 bond is on the opposite side of the ammonia molecule from the lone pair, it is unlikely that this contact is a hydrogen bond, and it is possible that this configuration does not occur.

Based on the number of equivalent configurations alone, the probabilities of the arrangements shown in Figs. 4(a), 4(b), and 4(c) are 4/8, 3/8, and 1/8, respectively. When the three arrangements are combined in these proportions the ratio between the occupancies of $\langle 111\rangle$ and $\langle 110\rangle$ D sites is 78:22—a value quite close to that obtained by free refinement (above).

The substitutional disorder of water and ammonia in the structure is interesting. Substitutional disorder has been observed in molecular systems (for example, nitrogen-oxygen), but seems to be confined to chemically similar systems and those with rotational disorder which can be explained on the basis of packing of spherical objects of similar radius. This is not the case for ammonia monohydrate. Ammonia and water are chemically very different, the molar volumes of ice VII (10.21 cm^3 [18]) and ammonia IV (14.4 cm^2 [15]) at 6.5 GPa differ by 40%, and there is good evidence to suggest that AMH VI is H-bonded. [The fact that the molar volume of AMH VI (11.6 cm^3) is smaller than the average of the molar volumes of ice and ammonia at the same temperature and pressure provides further evidence that AMH VI is H-bonded.] We have been unable to find any other example of substitutional disorder in an H-bonded system. AMH VI thus appears to be a new class of material—an H-bonded substitutionally disordered molecular alloy.

The AMH VI structure raises important new possibilities for planetary modeling studies. Substitutional disorder makes it possible to accommodate nonstoichiometry within the structure (at least on the water-rich side). Furthermore, the bcc configuration of molecular centers appears to be very stable, persisting to at least 150 GPa in ice VII [19]. It is thus possible that a single structure (effectively a solid solution of AMH VI and ice VII) covers all water-rich ammonia-water mixtures and that this phase has a wide range of stability in pressure, making it the relevant phase for planetary modeling. Also, the discovery of a second ice-VII-related structure in addition to $H_2 \cdot H_2O$ raises the possibility that variants of the bcc arrangement of molecular centers is the ultimate high-pressure structure of many water mixtures.

We acknowledge M. Guthrie and D. J. Francis for assistance during these experiments and S. Klotz for technical advice. This work is funded by the U.K. Engineering and Physical Sciences Research Council through research grants and by the U.K. Central Laboratory of the Research Councils through access to beamtime at the ISIS Facility and other support.

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