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Hydrogen bonding in ND_3 probed by neutron diffraction to 24 GPa

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The structure of deuterated ammonia has been determined as a function of pressure up to 24 GPa using powder neutron-diffraction techniques. The presence of an isostructural transition at approximately 18 GPa is confirmed and ascribed to a slight displacement of one D atom. As a result, the H bond formed by this D atom changes angle and becomes nearly straight (178°) at 24 GPa. A departure from the molecular C_{3v} symmetry is also detected which is further supported by the evolution of the Raman spectra.

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Hydrogen bonding is a complex interaction, whose strength varies widely from one species to the other. This strength depends on several factors such as the nature of the bonded anions, the distance between them, and the bond angle.[1] There have been large experimental and theoretical efforts in order to measure and rationalize the influence of these various factors and their correlations. High-pressure studies have proven to be a valuable tool in this regard as it allows one to study the H bonds in a single compound as a function of density, and thus variable bond length, while the other parameters remain fixed.

The principal difficulty of structural studies of H-bonded compounds at high pressure lies in the localization of the light H atoms. In this respect, a breakthrough was achieved by the development of high-pressure neutron-diffraction techniques (neutrons are much more sensitive to H/D atoms than x rays) and nowadays light compounds under pressures as high as 25 GPa can be studied with this technique.[2] In ice VIII, for example, the O-H length was studied as a function of pressure and found to increase less rapidly with decreasing O…O distance than for other H-bonded compounds studied at ambient pressure.[3] At higher pressure, the molecular nature of water ice disappears and a symmetric state where the proton is localized between two oxygen atoms has been predicted[4] and observed in the range of 60–90 GPa.[5–7] *Ab initio* calculations have evidenced the role of quantum effects (proton tunneling and zero-point motion) in this transition.[8] The pressure-induced symmetrizations of H bonds in HCl,[9] DCl,[10] and HBr (Ref. 11) have also been observed.

In ammonia, theoretical *ab initio* calculations[12,13] have revealed that if the orthorhombic $P2_12_12_1$ phase IV, produced above 4 GPa, remains stable, H-bond symmetrization is unlikely to occur before a few terapascals. However, the evolution of the bonding pattern in ammonia may be more complicated, as suggested by the recent theoretical work of Pickard and Needs.[14] Indeed, these authors predict that ammonia transforms above 90 GPa into a ionic solid consisting of alternate layers of NH_4^+ and NH_2^-. At 300 GPa, another ionic structure is predicted with some symmetric H bonding between the NH_2^- ions. At even higher pressures ($P > 440$ GPa), Pickard and Needs[14] find that another molecular phase is stable, characterized by strong bond-angle distortion. The structural and bonding evolutions of ammonia under pressure would therefore be very different than in water ice, which remains to be probed by experiment.

The up-to-date experimental phase diagram of ammonia is reported in Fig. 1. The structure of phase IV was solved using powder neutron-diffraction data on ND_3 (Refs. 2 and 16): it is fully ordered, with space group $P2_12_12_1$. The geometry of the H bonds in phase IV is more complex than in phase I (the ambient-pressure solid) since there are three nonequivalent H bonds. This structure was found compatible with single-crystal x-ray diffraction (XRD) data at room temperature[17] and Raman-scattering data at low temperature[18] for both NH_3 and ND_3. The neutron study showed that phase IV is stable up to 9 GPa at 300 K.[16] At higher pressures, Raman-scattering[19] and Brillouin-scattering[20] experiments on NH_3 provided evidence for a phase transition to phase V at 12–14 GPa and 300 K. Our x-ray diffraction experiments[17] have confirmed the presence of this phase transition in NH_3 and ND_3 and revealed that the high-pressure phase is isosymmetric to phase IV. Although this is a first-order transition, we have been unable to detect a volume jump at 300 K (Ref. 17) or a discontinuity on the III-IV transition line at the expected triple point.[21] A large isotopic effect has also been reported: the transition has been observed at 12 and 18 GPa, respectively, for NH_3 and ND_3 at

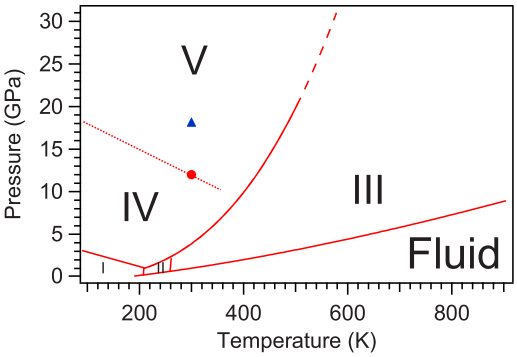

FIG. 1. (Color online) Phase diagram of ammonia according to Refs. 19, 21, and 22. The circle and triangle represent, respectively, the IV-V transition in NH_3 and ND_3 reported in Ref. 17.

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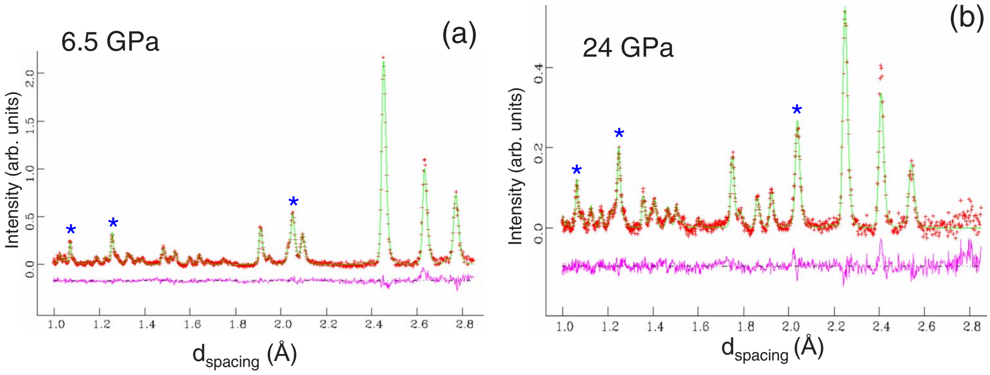

FIG. 2. (Color online) Powder neutron-diffraction data and Rietveld profile refinements of ND_3 at (a) 6.5 and (b) 24 GPa. Crosses are experimental data. The green continuous line is the calculated pattern. The stars indicate the reflections from the sintered diamond anvils. The difference between the observed and calculated profiles is shown at the bottom.

300 K. It was thus suggested that this phase transition is the result of changes in the positions of the H/D atoms.

The main purpose of this study is to determine the structure of ammonia, including the positions of the H atoms, to pressures higher than the IV-V phase transition. This has been achieved by performing powder neutron-diffraction experiments at room temperature. Due to the large incoherent cross section of H atoms, a ND_3 sample has been studied. This in turn required to reach pressures in excess of 18 GPa to pass the transition. We present here results obtained up to 24 GPa, showing the subtle role of H bonds in the mechanism of the transition.

High-pressure neutron-diffraction experiments were carried out in the Paris-Edinburgh (PE) press using the techniques described in Refs. 2 and 15. A ND_3 liquid sample (isotopic purity $\geq 99.66\%$) of 30 mm^3 was cryogenically loaded into sintered diamond anvils using a specifically designed clamp, which was inserted into the V7 PE press. Neutron-diffraction patterns were collected on the PEARL station of the ISIS spallation neutron source at the Rutherford Appleton Laboratory (U.K.).

To obtain a good powder sample of phase IV, the liquid sample was first cooled to 173 K to produce a polycrystal of phase I, then rapidly compressed to 6 GPa into the stability field of phase IV, and finally warmed up to room temperature. The similarity between the diffraction patterns collected on the nine modules of the detector bank indicated that this procedure produced a nearly texture-free sample of phase IV. This was further confirmed by the structural refinement as shown below.

Diffraction spectra, using the time-of-flight technique, were collected at five pressures (6.5, 15.3, 18.5, 21.6, and 24 GPa) and recorded for a few hours (6–7 h) at room temperature. The pressure was deduced from the volume of ND_3 using the equation of state determined in Ref. 17. Full profile Rietveld refinements were carried out using the GSAS package.[23] A two-phase refinement procedure was adopted to take into account the diffraction signal from both ND_3 and the diamond anvils. In addition to the phase fraction and background coefficients, a minimal set of variables was refined for each phase: the scale factor, the lattice parameters, internal coordinates (for ND_3 only), isotropic thermal parameters (one each for N and D), and two profile coefficients. The total number of refined parameters is 35. The refinement used all data with d spacing in the range of 0.5–3 Å, which include more than 400 reflections from ND_3.

Figure 2(a) shows the diffraction pattern collected at 6.5 GPa, along with the final Rietveld profile refinement. The space group ($P2_12_12_1$) and atomic positions determined by Loveday *et al.*[16] at 5 GPa were used as the initial model. An excellent fit was obtained (reduced χ^2 of 1.52) without the need to include a preferred orientation model. The refined parameters are $a=3.186\,8(5)$ Å, $b=5.543\,3(8)$ Å, and $c=5.255\,9(4)$ Å for lattice parameters; $x=0.242\,9(18)$, $y=0.349\,6(10)$, and $z=0.256\,2(10)$ for the N atom; 0.366 7(22), 0.177 9(21), and 0.231 0(18) for D_a; −0.046 9(34), 0.321 6(18), and 0.321 2(19) for D_b; and 0.211 4(33), 0.429 0(14), and 0.085 2(18) for D_c. The isotropic thermal factors are $U_{iso}(D)=0.028(2)$ Å^2 and $U_{iso}(N)=0.010(1)$ Å^2. This refined structure is nearly identical to that determined by Loveday *et al.*[16] at 5 GPa. In phase IV, the C_{3v} symmetry of the molecule is not constrained by the space group and a small dispersion of bond lengths and angles is observable (Fig. 3) as noted in Ref. 16. Nonetheless, the refinement is of similar quality if a rigid-body model, constraining all intramolecular bond lengths and angles to be equal, is used. There is thus no evidence for the loss of the molecular symmetry in phase IV, in agreement with Ref. 16 and *ab initio* calculations.[13] On the other hand, the three H bonds in phase IV are clearly nonequivalent. Finally, the very good agreement between our refined structure at 6.5 GPa and previous experimental work on one hand, and *ab initio* calculations on the other hand, confirms that our sample is of suitable quality for structural refinement.

On increasing pressure up to 24 GPa, no new peaks were detected in the diffraction patterns. High-quality refinements could be obtained in space group $P2_12_12_1$ at all pressures, using the same parameter set as at 6.5 GPa. The diffraction pattern and final profile refinement at 24 GPa are shown in Fig. 2(b).

Figure 3 shows the variations with pressure of the angles and lengths of the covalent and hydrogen bonds determined from the present work (see also Fig. 4 for atom labels). These data agree very well with previous ones[24] up to 9 GPa. Smooth variations of all bond distances and angles are observed up to 18 GPa. At this pressure, there is a clear change in the evolution of the angle of $N\ldots D_1\text{-}N_1H$ bond: whereas it is nearly constant up to 18 GPa, it starts to increase rapidly above this pressure. A similar change is observed on the $<D_bND_c$ internal angle and a closer look reveals that both effects are due to an anomalous evolution of the D_c atom position (and the symmetry equivalent D_1 atom) along the a axis.

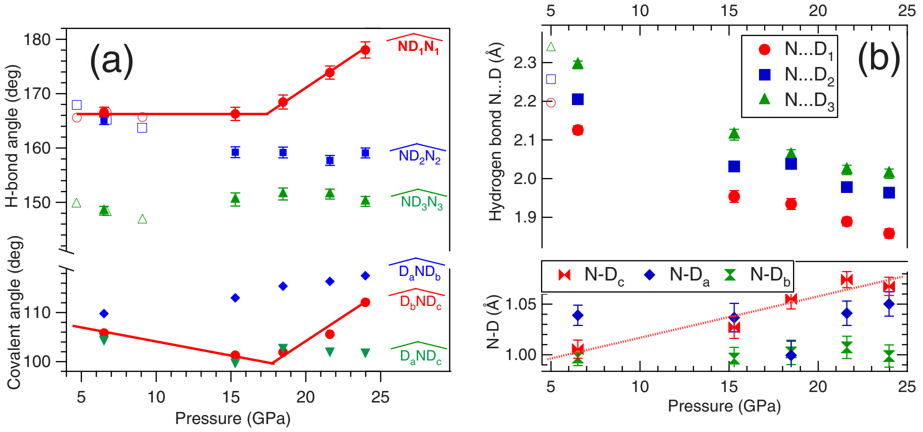

FIG. 3. (Color online) Evolution of the (a) bond angles and (b) lengths of the covalent and hydrogen bonds in ND_3 with pressure. Filled symbols are our experimental data and open symbols are previous experimental results (Ref. 24). Solid and dashed lines are guides for the eyes.

Figure 4 shows the refined structure at 24 GPa. At first glance, it is very similar to the one at 6.5 GPa. There is, however, a noticeable difference in the geometry of the $N\ldots D_1$-N_1 hydrogen bond: initially bent at 166.6(9)° at 6.5 GPa, the bond angle has become nearly straight at 24 GPa [178(1.5)°]. It is interesting to note that this H bond is the strongest one at low pressure since it is the shortest and least bent. Calculations of charge density along the bond confirmed this statement.[13]

The observed change in the behavior of the $N\ldots D_1$-N_1 bond precisely occurs at the pressure where our single-crystal XRD study[17] evidenced an isostructural transition in ND_3. In our XRD work, the main manifestations of the transition were the sudden splitting of the single crystal and a discontinuous change in the compressibility along the c axis (evidenced by a kink in the evolution of the c/a ratio vs pressure). The c/a ratio determined in the present work is in good agreement with x-ray data[17] although the fewer collected neutron data points do not allow us to evidence the kink observed by XRD. The present results thus suggest that this transition is related to the straightening of the $N\ldots D_1$-N_1 bond induced by the movement of the D_c ($\equiv D_1$) atom. Since this does not change the crystal symmetry, the space group of this high-pressure phase (which we will call V for homogeneity with previous works[19]) remains $P2_12_12_1$. As can be seen from Fig. 4, the $N\ldots D_1$-N_1 bond is mainly along the c axis. Its projection onto this axis amounts to ~82% of its length. The different bond geometry in phase V thus provides a likely explanation for the change in compressibility along c.

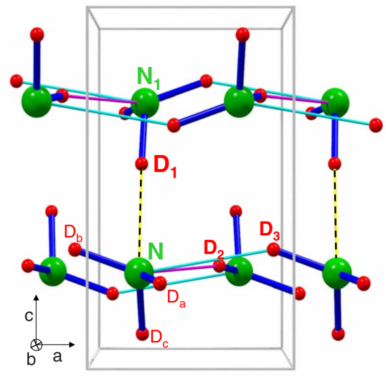

FIG. 4. (Color online) Structure of ND_3 determined at 24 GPa. Thin lines show hydrogen bonds, with the $N\ldots D_1$-N_1 bond emphasized by a dashed line. The refined parameters are $a=2.921\,5(5)$ Å, $b=5.092\,1(11)$ Å, and $c=4.805\,6(5)$ Å; $x=0.238\,8(22)$, $y=0.336\,3(15)$, and $z=0.255\,2(13)$ for the N atom; 0.350 8(29), 0.141 5(23), and 0.232 1(14) for D_a; −0.082 3(40), 0.314 5(21), and 0.322 6(21) for D_b; and 0.255 0(61), 0.455 9(22), and 0.073 1(20) for D_c. The thermal factors are $U_{iso}(D)=0.017(2)$ Å^2 and $U_{iso}(N)=0.005(1)$ Å^2.

We also observe a distortion of the internal structure of the ammonia molecule under compression. Figure 3(a) shows the variation of the intramolecular bond distances with pressure. The distance N-D_c seems to increase continuously with pressure with a slope of 0.004 1(7) Å/GPa, while the other covalent bond lengths are nearly constant up to 24 GPa [0.000 17(7) and 0.000 2(2) Å/GPa for N-D_a and N-D_b, respectively], a behavior which is more similar to that of the O-D bond in ice VIII (Refs. 3, 25, and 26) (0.000 40 Å/GPa for O-D up to 21 GPa). The lengthening of the N-D_c bond thus appears particularly large compared to that of the O-D bond in ice VIII in the same pressure range. We note, however, that if only the last three points above the transition at 18 GPa are considered the apparent lengthening rate reduces to 0.002(2) Å/GPa.

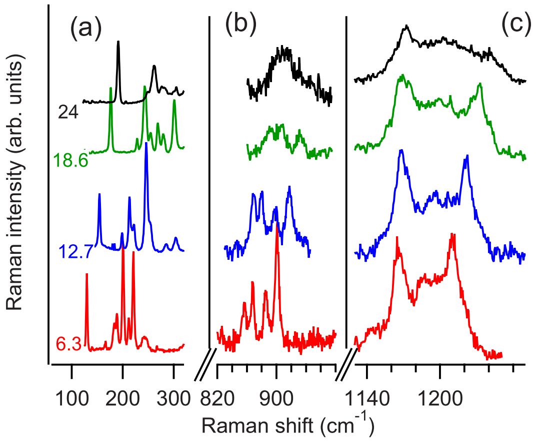

FIG. 5. (Color online) Evolution of the Raman spectra of the (a) lattice modes and bending modes (b) ν_2 and (c) ν_4 of ND_3 with pressure (in gigapascal) indicated on the left. These spectra were obtained using the same samples as described in Ref. 18.

The internal angle <DND of the molecule is also more distorted at 24 GPa: it is now dispersed between 102(1)° and 117.5(6)°. Such a distortion should induce a broadening of the internal vibrational modes of ammonia, and in particular those involving torsional motions of the molecules: ν_2 and ν_4. To verify this, we measured the Raman spectra of a single crystal of ND_3 at 80 K, using the same techniques as described in Ref. 18. As shown in Figs. 5(b) and 5(c), there is effectively a large broadening of these modes above 20 GPa. In particular, the four modes of ν_2 type[27] are well resolved at 6.3 GPa but form a single broad and weak band at 24 GPa. The bending modes ν_4 [Fig. 5(c)] and the stretching modes ν_1 and ν_3 (not shown) also broaden significantly above 20 GPa. In contrast, the lattice modes [Fig. 5(a)] do not exhibit such a strong broadening. We thus think that this phenomenon is related to the distortion of the molecule and not to nonhydrostatic conditions.[28] To check whether this distortion is reasonable around 20 GPa, we compared the energy gained from the isothermal compression to the energies of the first excited state of the molecule corresponding to the torsional modes ν_2 and ν_4. The former is obtained by integrating the equation of state of ND_3 up to 20 GPa (Ref. 17) and gives 1.19 eV per molecule, while the latter are approximately 0.11 and 0.15 eV for ν_2 and ν_4, respectively. At this first level of approximation, it is thus reasonable from an energy viewpoint that the compression distorts the molecule.

In conclusion, the present neutron-diffraction experiments have confirmed a subtle structural phase transition in ND_3 at ~18 GPa. This transition is induced by the movement of one D atom. As a consequence, the hydrogen bond formed by this atom and the neighboring molecule becomes nearly linear at 24 GPa, whereas the two other types of H bond seem unaffected by the transition. This is accompanied by an apparent distortion of the molecule compared to the lower-pressure phases. This increased anisotropy in the bonding scheme of ammonia contrasts with the case of H_2O where all H bonds are equivalent. This strengthens the idea that the structural and bonding patterns of ammonia in the 100 GPa range could be very different from that of water ice VIII and VII. The straightening as well as the rapid lengthening of the N-D_1 distance with pressure could make the symmetrization of the N…D_1-N_1 hydrogen bond easier than the other ones and thus achieved at lower pressures. Alternatively, this could signal a step toward the formation of the ionic compound NH_4^+ NH_2^- predicted by Pickard and Needs[14] at higher pressures.

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[1] A. Novak, *Structure and Bonding* (Springer, Berlin, 1974).

[2] S. Klotz, M. Gauthier, J. M. Besson, G. Hamel, J. S. Loveday, R. J. Nelmes, R. M. Wilson, and W. G. Marshall, Appl. Phys. Lett. **67**, 1188 (1995).

[3] R. J. Nelmes, J. S. Loveday, R. M. Wilson, J. M. Besson, P. Pruzan, S. Klotz, G. Hamel, and S. Hull, Phys. Rev. Lett. **71**, 1192 (1993).

[4] W. B. Holzapfel, J. Chem. Phys. **56**, 712 (1972).

[5] P. Pruzan, J. C. Chervin, and B. Canny, J. Chem. Phys. **99**, 9842 (1993).

[6] K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, Phys. Rev. B **54**, 15673 (1996).

[7] A. F. Goncharov, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, Phys. Rev. Lett. **83**, 1998 (1999).

[8] M. Benoit, D. Marx, and M. Parrinello, Nature (London) **392**, 258 (1998).

[9] K. Aoki, E. Katoh, H. Yamawaki, M. Sakashita, and H. Fujihisa, Physica B **265**, 83 (1999).

[10] E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki, Phys. Rev. B **61**, 119 (2000).

[11] E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki, Phys. Rev. B **59**, 11244 (1999).

[12] C. Cavazzoni, G. L. Chiarroti, S. Scandolo, E. Tosatti, M. Bernasconi, and M. Parrinello, Science **283**, 44 (1999).

[13] A. D. Fortes, J. P. Brodholt, I. G. Wood, and L. Vočadlo, J. Chem. Phys. **118**, 5987 (2003).

[14] C. Pickard and R. Needs, Nature Mater. **7**, 775 (2008).

[15] S. Klotz, J. M. Besson, G. Hamel, R. J. Nelmes, J. S. Loveday, W. G. Marshall, and R. Wilson, Appl. Phys. Lett. **66**, 1735 (1995).

[16] J. S. Loveday, R. J. Nelmes, W. G. Marshall, J. M. Besson, S. Klotz, and G. Hamel, Phys. Rev. Lett. **76**, 74 (1996).

[17] F. Datchi, S. Ninet, M. Gauthier, A. M. Saitta, B. Canny, and F. Decremps, Phys. Rev. B **73**, 174111 (2006).

[18] S. Ninet, F. Datchi, A. M. Saitta, M. Lazzeri, and B. Canny, Phys. Rev. B **74**, 104101 (2006).

[19] M. Gauthier, P. Pruzan, J. C. Chervin, and J. M. Besson, Phys. Rev. B **37**, 2102 (1988).

[20] M. Gauthier, P. Pruzan, J. C. Chervin, and A. Polian, Solid State Commun. **68**, 149 (1988).

[21] S. Ninet and F. Datchi, J. Chem. Phys. **128**, 154508 (2008).

[22] R. L. Mills, D. H. Liebenberg, and P. Pruzan, J. Phys. Chem. **86**, 5219 (1982).

[23] A. C. Larson and R. B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2004.

[24] J. S. Loveday, W. G. Marshall, R. J. Nelmes, J. M. Besson, S. Klotz, and G. Hamel, in *Proceedings of the Adriatico Research Conference, 1997*; http://users.ictp.it/~pub_off/sci-abs/smr999/51.pdf

[25] J. M. Besson, P. Pruzan, S. Klotz, G. Hamel, B. Silvi, R. J. Nelmes, J. S. Loveday, R. M. Wilson, and S. Hull, Phys. Rev. B **49**, 12540 (1994).

[26] R. J. Nelmes, J. S. Loveday, W. Marshall, J. Besson, S. Klotz, and G. Hamel, Rev. High Pressure Sci. Technol. **7**, 1138 (1998).

[27] In phase IV, the ν_2 and ν_4 modes have, respectively, four and eight components due to crystal-field splitting (see Ref. 18).

[28] We used a gold ring around the crystal to improve the hydrostaticity of compression. In the pressure range of the IV-V phase transition, no evidence for strong nonhydrostatic effects have been observed in our single-crystal x-ray diffraction experiments as reported in Ref. 17.