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X-ray Study of Solid Ammonia*

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Ammonia and deutero-ammonia have been studied by single-crystal and powder X-ray methods. There are four molecules in the cubic unit cell, and the space group is confirmed to be $P2_13$. The nitrogen parameter obtained by least-squares refinement is equal to 0·0401 for NH_3 at −102° C. and the same for ND_3 at −160° C. Cell dimensions, determined by powder methods, are: $a = 5{\cdot}084$ Å for NH_3 at −196 °C., 5·073 Å for ND_3 at −196 °C., 5·091 Å for ND_3 at −160 °C., and 5·138 Å for NH_3 at −102 °C. Each ammonia molecule is involved in six hydrogen bonds of approximate length 3·4 Å. A possible assignment of the hydrogen atoms to these bonds is given. Electron-density maps give evidence of hydrogen positions with coordinates (0·85, 0·14, 0·99), in agreement with this assignment, but with hydrogen off the bond axis, making the H–N–H angles more nearly tetrahedral.

Introduction

Earlier X-ray work on solid ammonia was done by powder methods. Reported values of the unit-cell dimension vary considerably, and new determinations by powder methods have been done on ordinary ammonia at −102 and −196 °C. and on deutero-ammonia at −160 and −196 °C. A single-crystal study has been undertaken to improve our knowledge of the atomic positions. The single-crystal work has been done on ordinary ammonia at −102 °C. and on deutero-ammonia at −160 °C. All the present work is concerned with the cubic form, as the new low-symmetric modification (Mauer & McMurdie, 1958) does not form under the conditions of these experiments.

Experimental

The ammonia and deutero-ammonia were distilled twice in a vacuum system and sealed in glass capillaries (diameter 0·1 to 0·2 mm.). The deutero-ammonia had, according to the specifications accompanying the cylinder, been made from magnesium nitride and 99·5% D_2O. The vacuum system was filled with deutero-ammonia and evacuated many times to eliminate most of the impurities containing hydrogen which would otherwise exchange with the heavy ammonia. In the mass-spectrometric analysis of samples from the original cylinder the mole percentage of ND_2H decreased gradually to below 9% after about 30 repeated fillings and evacuations of the spectrometer. This can be considered to correspond to a content of hydrogen of less than 3%. Samples from the X-ray capillaries gave less than 4% hydrogen. The effect on the unit-cell dimension due to this impurity is well within the limits of accuracy stated in this work.

The single crystals were grown in the ordinary way in a modified Weissenberg camera (Olovsson & Templeton, 1959). Equi-inclination Weissenberg photographs, layers 0 to 5, were taken with rotation about [110] at −102 ± 2 °C. of ordinary ammonia and at −160 ± 2 °C. of deutero-ammonia. The relative intensities were estimated visually by using multiple-film technique (four films) and comparing with an intensity scale. The data were corrected for the Lorentz and polarization effects. Because of the symmetry, equivalent reflections occur in several layers and permit good interlayer scaling.

The powder photographs (Debye–Scherrer type) were taken with the Weissenberg camera setup with some modifications of the film holder to get reflections of as high order as possible. By moving the film holder between each exposure it was possible to take a great number of photographs on the same film with a minimum disturbance of the film setting. Each powder picture was about 5 mm. wide, and the different pictures were immediately adjacent to one another. Exposures were located on the film in the following order: 1, quartz; 2, NH_3; 3 and 4, NH_3 and ND_3 on top of each other; 5, ND_3; 6, quartz; 7 and 8, NH_3

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and ND_3 on top of each other; 9, NH_3; 10, ND_3; 11, quartz. The powders were obtained by cooling the liquids in the capillaries quickly down to liquid nitrogen temperature. Exposures 2 and 3 were taken with the same powder, different from 7 and 9. Similarly, in exposures 4 and 5 the powder was different from 8 and 10. The quartz calibration photographs were zero-layer rotation pictures of a single crystal of quartz at 25 °C. Apart from these exposures calibrated photographs were also taken of NH_3 at −102 °C. and of ND_3 at −160 °C. All X-ray work was done with Cu $K\alpha$ and β radiation.

Unit cell

The difference in unit-cell dimensions of NH_3 and ND_3 is such that the separation of their lines is comparable to the separation of Cu $K\alpha_1$ and α_2. The isotope effect is therefore plainly visible for the higher-order reflections (powder lines up to $\theta = 80{\cdot}5°$ were obtained). The different individual values of the unit-cell dimensions, obtained from measurements of the higher-order reflections on which the accepted values are based, are given in Table 1 for the data from −196 °C. The values at the different temperatures may be summarized as follows:

$$\begin{aligned} NH_3:\ a &= 5{\cdot}138 \pm 0{\cdot}002 \text{ Å at } -102 \pm 2 \text{ °C.}, \\ & 5{\cdot}084 \pm 0{\cdot}001 \text{ Å at } -196 \pm 1 \text{ °C.}, \\ ND_3:\ a &= 5{\cdot}091 \pm 0{\cdot}002 \text{ Å at } -160 \pm 2 \text{ °C.}, \\ & 5{\cdot}073 \pm 0{\cdot}001 \text{ Å at } -196 \pm 1 \text{ °C.}, \end{aligned}$$

(Cu$K\alpha_1\lambda = 1{\cdot}54051$ Å, $\alpha_2\lambda = 1{\cdot}54433$ Å, $\beta\lambda = 1{\cdot}39217$ Å, $a = 4{\cdot}913$ Å for α quartz at 25 °C.).

Table 1. *Unit-cell dimension at* −196 °C. *determined from higher-order reflections*

$h^2+k^2+l^2$	a_{NH_3}	a_{ND_3}
37, α_1	5·0839 Å	5·0724 Å
37, α_2	5·0839	5·0733
38, α_1	5·0839	5·0739
38, α_2	5·0827	5·0729
41,* α_1	5·0835	5·0739
41, α_2	5·0835	5·0737
42, α_1	—	5·0725
42, α_2	—	5·0729

* 39 is impossible; 40 corresponds to {026}, {062}, neither of which was observed on the single-crystal photographs.

Vegard & Hillesund (1942) report an isotope effect of 0·010 Å, although the individual values for NH_3 and ND_3 (5·22(53) and 5·21(53) kX. resp.) differ quite considerably from the values in this investigation (see further below). With their method of obtaining the powder (condensing gaseous ammonia on a copper rod at −185 °C.) it is in principle possible that they got some of the new low-symmetric form (Mauer & McMurdie, 1958), but they do not mention how closely their lines fit cubic indexing.

Using the values of the investigation reported herein, one calculates the mean linear expansion coefficient of NH_3 between −102 and −196 °C. to be $11{\cdot}2 \pm 0{\cdot}5 . 10^{-5}$/°C. and that of ND_3 between −160 and −196 °C. to be $9{\cdot}8 \pm 1{\cdot}0 . 10^{-5}$/°C. McKelvy & Taylor (1923) report a mean linear expansion coefficient of $7 . 10^{-5}$/°C. for NH_3 in the interval −79 to −185 °C. based on the densities determined at those two temperatures. Using the value $9{\cdot}8 . 10^{-5}$/°C. as expansion coefficient between −160 and −196 °C. for NH_3, and referring earlier published data to −196 °C., changing in all cases to Ångström units, one obtains the values collected in Table 2.

Table 2. *Reported unit-cell dimensions of* NH_3

Temp.	a (kX.)	a (Å) at −196 °C.*	Reference
−185 °C.	5·19	5·19(5)	Mark & Pohland (1925)
−185	5·12	5·12(5)	De Smedt (1925)
−170	5·08	5·07(7)	Natta & Casazza (1930)
−185	5·22(53)	5·23(02)	Vegard & Hillesund (1942)
−196	—	5·084	This work

* Calculated as described in the text.

Space group

The data showed the diffraction symmetry of the cubic Laue group $m3$. Systematic absences were: $h00, 0k0, 00l$ for h, k, l odd ($h, k, l = 0$ to 6). This suggests the space group $P2_13(T^4)$, but the space groups $P23$ and $Pm3$ are also possible, if the absences are assumed to be caused by special arrangement of the atoms. It turns out to be impossible to get any reasonable trial structure in agreement with the data by using $P23$ or $Pm3$. The structure obtained by using $P2_13$ gives good agreement with the data; this fact shows this choice to be correct. This space group is in agreement with the earlier results (de Smedt, 1925; Mark & Pohland, 1925). With four molecules per unit cell, the calculated density of NH_3 is 0·834 g.cm.$^{-3}$ at −102 °C. and 0·861 at −196 °C., for ND_3 equal to 1·009 at −160 °C. and 1·020 at −196 °C. McKelvy & Taylor (1923) determined the density picnometrically to be 0·817 at −79 °C. and 0·836 at −185 °C. for NH_3. The nitrogen atoms are then located on the threefold axes corresponding to the fourfold positions:

$$(x, x, x);\ (\tfrac{1}{2}+x, \tfrac{1}{2}-x, \bar{x});\ (\bar{x}, \tfrac{1}{2}+x, \tfrac{1}{2}-x);\ (\tfrac{1}{2}-x, \bar{x}, \tfrac{1}{2}+x) .$$

The nitrogen parameter

In the following calculations the single-crystal data of NH_3 at −102 °C. and ND_3 at −160 °C. were each used separately. Using a couple of reflections, one finds that the nitrogen coordinate x is close to 0·040. The coordinate and isotropic temperature factor for nitrogen and the scale factor were then refined by least-squares methods on the IBM 650 computer. In the first cycles only the temperature factor and scale factor were refined and the coordinate kept constant. R_3 (see below) was the quantity actually minimized. The weighting factor w in this expression and some other details of the program are described elsewhere (Olovsson & Templeton, 1959). The original 'L.S. II' program was modified for this special structure. One notices, for example, that the derivatives for atoms in special (fourfold) positions have to be formulated differently than those for atoms in general (twelvefold) positions. This is of course true also for other cubic, hexagonal, and tetragonal space groups when two or more of the coordinates x, y, z are equal by symmetry. The scattering factors for nitrogen (N^0) are those published by Berghuis *et al.* (1955). The shifts in the parameter x in the final cycles were less than 0·0001. The results, together with the standard deviations, after about 20 cycles of refinement were:

NH_3 at −102 °C.:

$$R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0{\cdot}103\ ,$$

$$R_2=[\Sigma(|F_o|-|F_c|)^2/\Sigma|F_o|^2]^{\frac{1}{2}}=0{\cdot}129\ ,$$

$$R_3=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}=0{\cdot}143\ ,$$

$$x=0{\cdot}0401\pm0{\cdot}0006;\quad B=1{\cdot}84\ \text{Å}^2.$$

ND_3 at −160 °C:

$$R_1=0{\cdot}071\ ,$$

$$R_2=0{\cdot}072\ ,$$

$$R_3=0{\cdot}081\ ,$$

$$x=0{\cdot}0401\pm0{\cdot}0005;\quad B=2{\cdot}85\ \text{Å}^2.$$

The observed and calculated structure factors are compared in Table 3. The reflections (002) and (111) appeared to suffer considerably from extinction effects in the case of NH_3 and were not included in the final refinements for that compound. R_1 when these reflections were included was 0·14. The crystal of ND_3 was somewhat less perfect (noticeable on the photographs), and the extinction effects accordingly seem to be quite small.

Finally, the scale factor, nitrogen temperature factor, and nitrogen coordinate were refined with each set of data with hydrogen included in the calculations. The hydrogen temperature factor was arbitrarily taken as 6·0 Å². When hydrogen was placed on the lines between the nitrogen atoms at 1·01 Å from nitrogen (as in Fig. 1) R_1 increased to 0·105 for NH_3 and to 0·077 for ND_3. When the hydrogen coordinates (0·85, 0·14, 0·99) obtained from a difference synthesis as described below were used instead, R_1 decreased to 0·097 for NH_3 and to 0·069 for ND_3. The atomic coordinate of nitrogen did not change during these refinements; the temperature factor changed to 1·75 Å² for NH_3 and to 2·10 Å² for ND_3. The fact that the 'temperature factor' for ND_3 (which was studied at a lower temperature) is larger than that for NH_3 calls attention to the obvious fact that this parameter includes many effects other than that of the amplitude of thermal vibration.

Table 3. *Observed and calculated structure factors*

	NH_3		ND_3	
hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$\lvert F_o\rvert$	$\lvert F_c\rvert$
002	10·7	15·2	15·4	14·8
004	4·1	4·0	3·6	3·6
006	< 0·9	0·2	< 0·5	0·2
011	5·2	5·3	5·5	5·2
012	6·4	7·4	6·5	7·2
013	3·5	2·0	3·0	1·8
014	5·7	5·8	5·2	5·3
015	< 1·1	0·4	0·6	0·3
016	3·2	3·5	2·4	2·8
021	1·4	1·9	1·3	1·9
022	8·1	9·4	8·7	9·0
023	3·1	2·9	2·4	2·7
024	2·9	2·9	2·5	2·6
025	2·5	2·1	1·9	1·8
026	< 0·7	0·2	< 0·3	0·1
031	6·4	7·1	6·7	6·6
032	2·8	3·1	2·3	2·8
033	4·4	3·4	3·8	3·0
034	3·5	3·2	2·7	2·7
035	1·1	0·8	0·9	0·7
041	1·9	1·5	1·6	1·4
042	3·0	2·9	2·6	2·6
043	3·7	3·0	2·8	2·6
044	1·1	1·2	0·9	1·0
045	2·0	2·6	1·8	2·1
051	4·9	4·6	3·8	3·9
052	1·1	0·7	< 0·5	0·6
053	2·7	2·7	2·3	2·2
054	0·8	0·8	0·7	0·7
061	1·1	0·9	0·5	0·7
062	< 0·7	0·2	< 0·3	0·1
111	10·9	17·6	16·8	17·2
112	3·5	3·5	3·0	3·4
113	6·5	6·8	6·0	6·4
114	1·8	1·7	1·5	1·5
115	1·9	1·4	1·2	1·2
116	1·0	0·9	0·7	0·7
122	5·8	4·9	5·0	4·6
123	5·0	4·9	4·4	4·5
124	2·7	1·9	2·2	1·6
125	3·5	3·5	2·9	2·9
126	0·9	0·7	0·5	0·6
132	3·2	3·0	2·7	2·7
133	3·5	3·4	3·0	3·0
134	3·3	2·9	2·6	2·4
135	1·0	1·0	0·8	0·8
142	4·4	4·3	4·0	3·8
143	2·1	1·9	1·6	1·6
144	2·0	1·8	1·6	1·5
145	1·5	1·6	1·2	1·2
152	2·2	2·0	1·8	1·6
153	1·0	1·0	0·9	0·8
154	1·9	2·5	1·6	1·9
162	2·3	2·8	1·9	2·2
222	6·5	6·3	5·8	5·9
223	3·3	3·0	2·7	2·7
224	2·6	2·4	2·3	2·1
225	2·0	1·7	1·6	1·4
233	3·2	2·9	2·8	2·5
234	2·8	2·6	2·1	2·2
235	1·4	1·4	1·1	1·1
243	2·7	2·4	2·2	2·1
244	1·6	1·6	1·3	1·3
253	2·0	2·2	1·7	1·7
333	2·4	2·4	2·6	2·1
334	2·2	2·0	1·7	1·6
344	1·3	1·5	1·2	1·2

Discussion of the structure

The structure can be roughly described as slightly deviating from face-centered cubic. If the nitrogen atoms were at $x=0$ and the ammonia molecules were spherically symmetric—e.g., rotating—the structure would be strictly close-packed. This would also imply no directed hydrogen bonds. However, in the structure under consideration, each nitrogen atom has only six closest neighbors, all at about 3·4 Å, and the other six have moved further away to about 3·9 Å (3·96 Å in NH_3, 3·92 in ND_3). The six closest neighbors to the nitrogen atom (N_0) at (0·0401, 0·0401, 0·0401) are shown in Fig. 1. Here N_1, N_2, and N_3 are related to one another by the threefold axis passing through N_0, and similarly with N_4, N_5, and N_6. The bond distances and angles are:

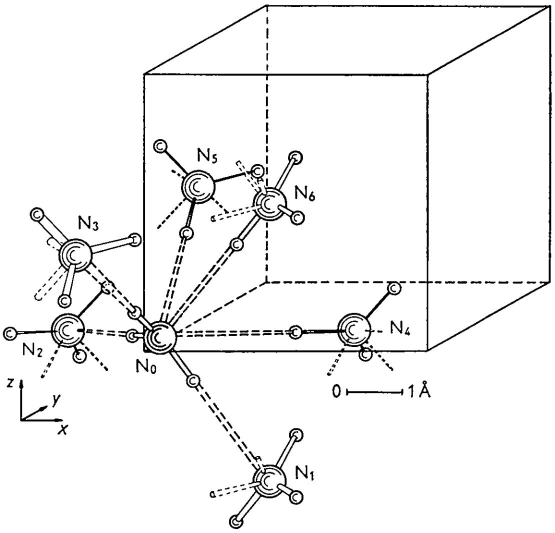

Fig. 1. The crystal structure of cubic ammonia. Only the six closest neighbors to the atom at (0·04, 0·04, 0·04) are shown. The hydrogen atoms are for simplicity placed on the lines between the nitrogen atoms, although there is experimental evidence that they are somewhat off these lines.

	for NH_3 at −102 °C.	for ND_3 at −160 °C.
$N_0N_1=N_0N_2\cdots N_0N_6$	3·380 ± 0·004 Å	3·349 ± 0·003 Å
$N_2N_0N_1=N_3N_0N_1=N_3N_0N_2$	118·05° ± 0·06°	118·05° ± 0·05°
$N_5N_0N_4=N_6N_0N_4=N_6N_0N_5$	71·66° ± 0·19°	71·66° ± 0·16°

One notices that the angles involving the first three neighbors are fairly close to the tetrahedral value. The most obvious interpretation of these facts is to assign the hydrogen atoms to nitrogen as in Fig. 1. The free electron pair is then used to form three hydrogen bonds. This may explain the long hydrogen bonds. This is analogous to the interpretation of the structure of ammonia monohydrate (Olovsson & Templeton, 1959), according to which one free-electron pair of the water molecule is used to form three hydrogen bonds, O · · · N–H, of 3·21, 3·26, and 3·29 Å.

The interpretation above is apparently inconsistent with inversion of the ammonia molecule of the type occurring in the gaseous state, as this would make the bonding situation (and therefore bond angles) to the neighbors N_1, N_2, and N_3 equivalent to those involving N_4, N_5, and N_6. This is of course quite unlikely also when it is considered that, with all hydrogen atoms involved in hydrogen bonds, inversion of one ammonia molecule means breaking of hydrogen bonds and has to be accompanied by simultaneous inversion of all the other molecules throughout the crystal. Infrared investigations (Reding & Hornig, 1951) show no indication of inversion in the solid state.

It is evident that rotation around the threefold axis of the ammonia molecule also implies breaking of hydrogen bonds. Such rotation should therefore be quite restricted. Heat-capacity data from 15 °K. up to the melting point (Overstreet & Giauque, 1937) give no indication of any transition that would probably be demanded if relatively unrestricted rotation occurred above a certain temperature. The excellent agreement between the entropies calculated from calorimetric and spectroscopic data also rule out transition in the interval 0 to 15 °K., not covered by the heat-capacity measurements. In agreement with this, X-ray powder work by Mauer & McMurdie (1958) indicate no phase changes as the cubic form is cooled down to liquid helium temperature. Compare these results with the situation in ammonia hemihydrate at −95 °C. (Siemons & Templeton, 1954). Here one of the two nonequivalent ammonia molecules is involved in only one hydrogen bond and therefore has great rotational freedom. When this compound is cooled down, the heat-capacity curve (Hildenbrand & Giauque, 1953) indicates a transition at about 50 °K. This is probably due to transformation to another structure in which the restriction to rotation of this ammonia molecule is much stronger, e.g., because its hydrogen atoms are involved in hydrogen bonds.

Ammonia might seem to be a favorable case in which to try to find the hydrogen atoms in the Fourier maps, e.g., F_o or (F_o-F_c) syntheses based on the nitrogen atoms only. However, the structure is noncentric, and the phases based on the nitrogen atoms only are obviously not quite correct in general. Only reflections for which one of the indices (h, k, l) is equal to zero get just the correct phase. Also, the unit cell is small, which means that there are very few reflections of low enough $\sin\theta/\lambda$ that the hydrogen contribution to the scattering is of importance. It was therefore somewhat surprising that the difference maps showed very definite maxima close to those places expected for the hydrogen atoms according to the discussion

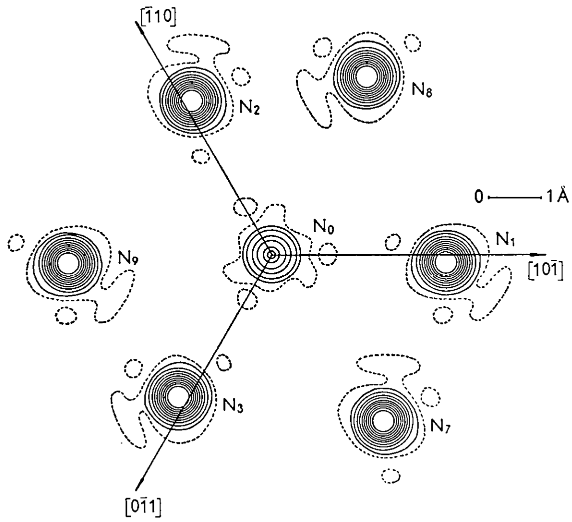

Fig. 2. Electron-density section (based on nitrogen only) along (111) passing through the origin. The atoms marked N_7, N_8, and N_9 are three of the six next nearest neighbors at 3·9 Å from N_0. The solid contours are drawn at 1, 2, 3, . . . e.Å^{-3}. Dotted contours correspond to $\frac{1}{2}$ e.Å^{-3}.

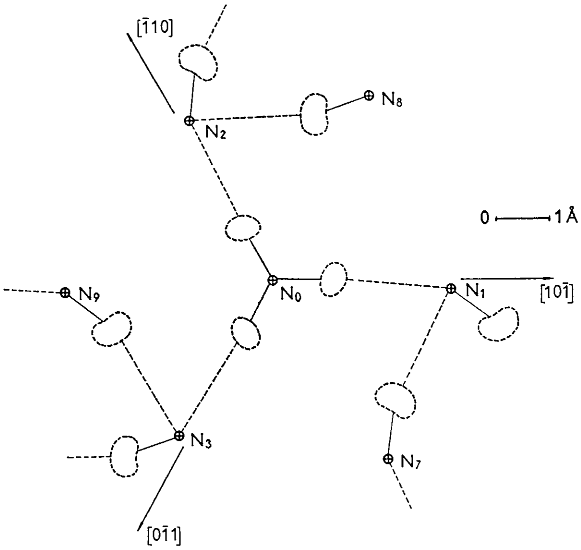

Fig. 3. Difference synthesis corresponding to Fig. 2. The dotted contours correspond to $\frac{1}{2}$ e.Å^{-3}.

above. No other peaks as large as these appeared in the whole three-dimensional difference synthesis. Some small extra maxima in the F_o synthesis thus turned out to be diffraction effects. Fig. 2 shows the electron-density section (based on nitrogen only) along (111) passing through the origin; Fig. 3 shows the corresponding difference synthesis. The maps shown are based on the data for ND_3, but the data for NH_3 give just the same features. This section passes approximately through the places where the hydrogen atoms of N_0 should be. The bonds between N_0 and its closest neighbors N_1, N_2, N_3 (Fig. 3), when looked upon from the side (looking perpendicular to the threefold axis), appear just like the bonds shown between N_1, N_2, N_3 and N_7, N_8, N_9. The hydrogen peaks are obviously somewhat off the lines between the nitrogen atoms. The hydrogen atoms shown in Fig. 1 are, for simplicity, placed just on the lines connecting the nitrogen atoms, at 1·01 Å from N_0. The angles $N_2N_0N_1$, $N_3N_0N_1$, and $N_2N_0N_3$ were given earlier as 118·1°. The angles between the threefold axis passing through N_0 and the lines N_0N_1, N_0N_2, N_0N_3 respectively are 98·1°. The ammonia molecule would obviously be quite distorted if the hydrogen atoms were located on the connecting lines. Using instead the hydrogen coordinates obtained from the difference map (0·85, 0·14, 0·99), one calculates the angles HN_0H' to be 107° and the angles between the threefold axis and the lines N_0H to be 111°. These angles are much closer to the tetrahedral value, and strengthen the confidence in these hydrogen coordinates. The nitrogen–hydrogen distance (1·13 Å for NH_3, 1·12 Å for ND_3) is considerably longer than the distance reported in the gas phase, 1·008 Å (Tables of interatomic distances, 1958), but somewhat longer distance is of course to be expected in the hydrogen-bonded solid.

The Fourier calculations were made with the IBM-701 computer at the University of California Computer Center.

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