

- HORIUCHI, S., MATSUI, Y. & BANDO, Y. (1976). *Jpn. J. Appl. Phys.* **15**, 2483–2484.
- JEANNIN, Y. (1962) *Ann. Chim. (Paris)*, **7**, 57.
- JELLINEK, F. (1957). *Acta Cryst.* **10**, 620–628.
- MORET, R., HUBER, M. & CÔMES, R. (1976). *Phys. Status Solidi, A*, **28**, 695–700.
- NAKAZAWA, H., MORIMOTO, N. & WATANABE, E. (1975). *Am. Mineral.* **60**, 359–366.
- NORRBY, L. J. & FRANZEN, H. F. (1970). *J. Solid State Chem.* **2**, 36–41.
- PIERCE, L. & BUSECK, P. R. (1974). *Science*, **186**, 1209.
- WADSLEY, A. D. (1957). *Acta Cryst.* **10**, 715–716.

*Acta Cryst.* (1979). A **35**, 569–571

## The Crystal Structure of Deuteroammonia between 2 and 180 K by Neutron Powder Profile Refinement

BY A. W. HEWAT AND C. RIEKEL

*Institut Max von Laue–Paul Langevin, BP 156 X, Grenoble, France*

(Received 28 December 1978; accepted 9 February 1979)

### Abstract

The structure of ND<sub>3</sub> has been refined by neutron powder profile analysis at 2, 77 and 180 K to a resolution of  $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$ . No orientational phase transition was found in this range. However, even at 2 K, a strong librational motion exists. The N–D bond length, after correction for libration, is constant with temperature (1.06 Å), as are the D–N–D angles ( $107.5 \pm 0.2^\circ$ ). This bond length is 5% longer than that found in the free molecule, because of hydrogen bonding, but the bond angles are virtually identical.

### Introduction

Solid ammonia has one of the simplest molecular structures. The molecules are bound together by rather weak hydrogen bonds involving the lone pair of electrons, which with the three H atoms make up an almost regular rigid tetrahedron around the N atom (Olovsson & Templeton, 1959; Reed & Harris, 1961).

NH<sub>3</sub> in its solid state is an ideal material for the study of the dynamics of simple molecular crystals. Righini & Klein (1978) have set up a lattice-dynamical model, which has been used by Dolling, Powell & Pawley (1978) to explain their inelastic neutron scattering results. Such model calculations require a precise knowledge of the structure, and this was one justification for the present study.

### The structure of NH<sub>3</sub> and ND<sub>3</sub>

Olovsson & Templeton (1959) studied single crystals of NH<sub>3</sub> and ND<sub>3</sub> by photographic X-ray techniques at 77 and 113 K. A neutron powder diffraction study of ND<sub>3</sub> was made by Reed & Harris (1961) at 77 K. Both

studies were limited by rather low resolution, *i.e.*  $\sin \theta/\lambda = 0.58 \text{ \AA}^{-1}$  (Olovsson & Templeton) and  $0.46 \text{ \AA}^{-1}$  (Reed & Harris). However, both agreed on the space group *P2<sub>1</sub>3* (*T*<sup>4</sup>) in which the atoms are placed as follows: 4 N at *u,u,u* with *u*  $\simeq 0.21$ ; 12 H at *x,y,z* with *x*  $\simeq 0.37$ , *y*  $\simeq 0.26$ , *z*  $\simeq 0.11$ . The refined coordinates (Table 1) agree within the rather large experimental errors.

### Experiment

The experiment was performed in two parts, both on the D1A high-resolution powder diffractometer (Hewat & Bailey, 1976) using a He gas flow cryostat. For the first part, data were collected at 77 K with a wavelength of 1.5 Å up to  $\sin \theta/\lambda = 0.66 \text{ \AA}^{-1}$ . Later, more precise results were collected at 2 and 180 K with a wavelength of 1.17 Å to extend the resolution to  $\sin \theta/\lambda = 0.85 \text{ \AA}^{-1}$ .

ND<sub>3</sub> (Saclay, 99% deuterated) was purified over Na and distilled. Some difficulties were experienced in preparing the powder sample. In the first attempt, ND<sub>3</sub> was sublimed from a solid-CO<sub>2</sub>-cooled reservoir into a liquid-N<sub>2</sub>-cooled vacuum-tight vanadium can. However, even at 77 K the intensities of some lines in the neutron diffraction pattern changed within a few hours, indicating the growth of crystallites in the sample. A similar effect was found when liquid ND<sub>3</sub> was snap frozen to 77 K. Finally, liquid ND<sub>3</sub> was frozen into a mortar immersed in a bath of liquid N<sub>2</sub> in a dry glove bag. It was then relatively easy to crush the solid ND<sub>3</sub> into a fine powder and to fill the vanadium can which was also cooled to liquid N<sub>2</sub> temperature. The can with about 6 g of ND<sub>3</sub> was transferred to the cryostat while still cold, and the temperature raised briefly to boil off any remaining N<sub>2</sub>. Careful checks for preferred orientation during the experiments revealed

Table 1. Parameters for solid ND<sub>3</sub> at 2, 77 and 180 K together with those found by Reed & Harris (1961) at 77 K, and Olovsson & Templeton (1959)

The thermal ellipsoids  $B_{ij}$  defined by the temperature factor  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + kl\beta_{23})]$ , where  $\beta_{ij} = \frac{1}{4}a_i^*a_j^*B_{ij}$ , are oriented with axes perpendicular to and along the (N-D) bonds (Fig. 2), and indicate strong libration even at 2 K. After correction for this libration, the N-D bond length increases by up to 0.069 Å, becoming (N-D)<sub>o</sub>. Refinements of the occupation number  $n_D$  for D shows that, with the assumed scattering lengths  $b_N = 0.940$  and  $b_D = 0.667$ , the sample was completely deuterated. The  $R$  percentage factors for integrated reflexions  $R_I$  and profile intensities  $R_p$  have their usual meanings and show that good agreement was obtained with the data, especially at 2 K. The  $R_p$  factor expected for purely statistical errors is  $R_E$ .

	2 K	77 K	180 K	Reed & Harris (77 K)	Olovsson & Templeton (113 K)
$\lambda$ (Å)	1.1655	1.4951	1.1655		
$a_o$ (Å)	5.048	5.073*	5.125		
$x_N$	0.2109 (3)	0.2108 (11)	0.2107 (7)	0.2127 (21)	0.2099 (5)
$x_D$	0.3750 (3)	0.3694 (13)	0.3689 (6)	0.3740 (19)	0.40
$y_D$	0.2712 (4)	0.2694 (10)	0.2671 (6)	0.2632 (37)	0.26
$z_D$	0.1129 (3)	0.1141 (11)	0.1159 (7)	0.1094 (16)	0.11
N-D (Å)	1.012 (2)	0.988 (9)	0.989 (5)	1.005 (23)	1.12
(N-D) <sub>o</sub> (Å)	1.061 (5)	1.039 (20)	1.058 (8)		
$\angle$ D-N-D (°)	107.5 (2)	108.0 (7)	107.8 (4)	110.4 (2.0)	107
D...N (Å)	2.357 (2)	2.393 (9)	2.425 (5)	2.374 (28)	
N-N (Å)	3.325 (2)	3.342 (8)	3.375 (5)	3.352 (11)	
$\angle$ ND...N (°)	160.0 (2)	160.7 (6)	160.3 (4)		

\* This lattice dimension (Olovsson & Templeton) was used to determine the neutron wavelength.

Table 1 (cont.)

	2 K	77 K	180 K
$B_{ii}$ (N) (Å <sup>2</sup> )	0.80 (3)	2.29 (18)	3.03 (6)
$B_{ij}$ (N) (Å <sup>2</sup> )	-0.04 (3)	-0.12 (12)	-0.11 (4)
$B_{11}$ (D) (Å <sup>2</sup> )	1.76 (7)	3.69 (29)	4.54 (13)
$B_{22}$ (D) (Å <sup>2</sup> )	2.13 (9)	3.22 (30)	5.60 (16)
$B_{33}$ (D) (Å <sup>2</sup> )	2.14 (7)	4.36 (24)	5.34 (17)
$B_{12}$ (D) (Å <sup>2</sup> )	-0.28 (5)	-0.76 (17)	-1.47 (9)
$B_{13}$ (D) (Å <sup>2</sup> )	0.56 (6)	0.72 (27)	0.74 (11)
$B_{23}$ (D) (Å <sup>2</sup> )	0.18 (6)	-0.22 (19)	-0.23 (11)
$u$ (N) (Å)	0.096	0.161	0.189
	0.103	0.175	0.199
	0.103	0.175	0.199
$u$ (D) (Å)	0.125	0.182	0.207
	0.169	0.214	0.257
	0.179	0.252	0.295
$n_D$	1.013 (13)	1.007 (55)	1.003 (22)
$R_I$ (%)	2.24	3.28	6.17
$R_p/R_E$	9.56/3.41	13.16/4.71	17.53/12.42

### Refinement and results

The profile-refinement program (Rietveld, 1967), modified for anisotropic vibrations (Hewat, 1973), was used for all three scans. No correction for preferred orientation or absorption was deemed necessary. Each point in the diffraction pattern was weighted according to the number of counters contributing and the average count. For such a simple structure on a high-resolution machine, it was easy to measure precisely the background between the peaks, even at the highest scattering angles: this was important for the refinement of the Debye-Waller factors.

As expected, the best fit to the observed profile was obtained at the lowest temperature (Fig. 1); at higher temperatures, the large ND<sub>3</sub> librations are not so well described by the usual second-order tensor of  $B_{ij}$ . The fit at 2 K is really very good, corresponding to a value

none, and this was confirmed on refinement to low  $R$  values without preferred-orientation corrections.

The data were collected by sweeping the bank of six counters from 6 to 160° in steps of 0.05° ( $2\theta$ ), taking about 22 h for the entire experiment. The results were corrected for small differences in the relative efficiencies, and the different counters added together to give a single pattern covering the entire angular range of measurements. Some weeks later, the experiment was repeated at 2 and 180 K with a new sample and the shorter wavelength. By this time all ten counters were operational, and the extra efficiency compensated for the lower intensity with the shorter wavelength.

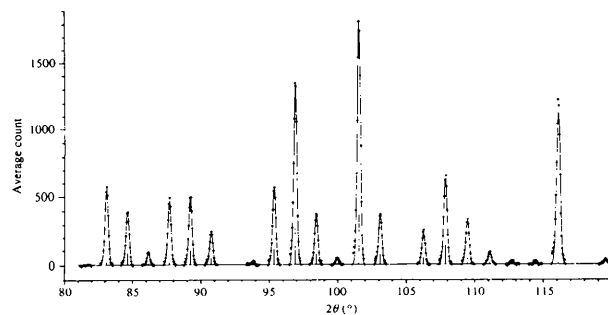


Fig. 1. The observed and calculated diffraction profiles for solid deuterioammonia at 2 K. The full pattern extends from 0 to 160°.

of about 1.1% for the  $R$  factor for structure factors usually quoted by crystallographers. The calculated errors for the parameters are also smallest at 2 K and largest at 77 K, where the data do not extend so far in  $\sin \theta/\lambda$ . No constraints were applied to any of the parameters, so that, for example, six independent  $B_{ij}$  factors were refined for the D atom. Nevertheless, the calculated thermal ellipsoids are physically reasonable, with their axes aligned almost along and perpendicular to the N–D bond.

The librational motion of the molecule is evident in Fig. 2. The magnitude of this libration is large even at 2 K, but none of the vibrational amplitudes increases as quickly with temperature as would be required for purely harmonic oscillators. We note that the barrier to  $C_3$  rotation has been estimated to be as low as 7.32 kJ mol<sup>-1</sup> (Rabideau & Waldstein, 1966) which would allow relatively rapid ( $\sim 10^6$  Hz) quantum-mechanical tunneling of the protons even at 2 K (Stejskal & Gutowsky, 1958). This might explain the observed deviation from a purely harmonic oscillator. Note also that the N–D...N bond is a little longer than that expected for a static hydrogen bond between N atoms.

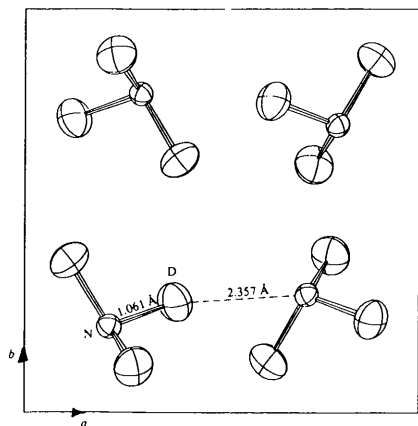


Fig. 2. ORTEP plots (Johnson, 1965) of the thermal ellipsoids of  $\text{ND}_3$ , showing strong well defined librations, even at 2 K. These relatively large ellipsoids, and the fact that the amplitudes increase less quickly with temperature than expected for a simple harmonic oscillator, may indicate quantum-mechanical tunneling of the protons.

A correction to the N–D bond length is necessary owing to the strong librational motion (Bacon, 1963). Table 1 shows the r.m.s. amplitudes of displacement in the directions of the axes of the ellipsoids; for the deuterons, the axes of strongest vibration are approximately perpendicular to the N–D bond, so that after subtraction of the translational vibration of the complete molecule, these displacements give the librational amplitudes needed for the bond-length correction. Since these corrections are relatively large (between 0.05 and 0.07 Å) the N–D bond is lengthened by about 5% in the solid from the value of 1.012 Å found for  $\text{ND}_3$  gas (Herzberg, 1966). This is a consequence of hydrogen bonding in the solid.

The uncorrected bond length is in good agreement with that found by Reed & Harris, but our D–N–D bond angle of  $107.5 \pm 0.2^\circ$  is much closer to that found for the gas than is their less precise value of  $110.4 \pm 2.0^\circ$ .

### References

- BACON, G. E. (1963). *Applications of Neutron Diffraction in Chemistry*. Oxford: Pergamon Press.
- DOLLING, G., POWELL, B. M. & PAWLEY, G. S. (1978). *Dynamics of Solid Ammonia*. Workshop on Dynamics in Molecular Crystals, Institut Laue–Langevin, 16–17 October.
- HERZBERG, G. (1966). *Electronic Structure of Polyatomic Molecules. Part III. Electronic Spectra*. Princeton, New York: Van Nostrand, Reinhold.
- HEWAT, A. W. (1973). *J. Phys. C*, **6**, 2559–2572.
- HEWAT, A. W. & BAILEY, I. (1976). *Nucl. Instrum. Methods*, **137**, 463–471.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- OLOVSSON, J. & TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 832–836.
- RABIDEAU, S. W. & WALDSTEIN, R. (1966). *J. Chem. Phys.* **45**, 4600–4603.
- REED, J. W. & HARRIS, P. M. (1961). *J. Chem. Phys.* **35**, 1730–1737.
- RIETVELD, H. M. (1967). *Acta Cryst.* **22**, 151–152.
- RIGHINI, R. & KLEIN, M. L. (1978). *J. Chem. Phys.* **68**, 5553–5557.
- STEJSKAL, E. O. & GUTOWSKY, A. S. (1958). *J. Chem. Phys.* **28**, 388–396.