

calculate coupling constants of 5.5 and 0.2 c.p.s. The first is in very good agreement with  $J_1$ .

Our thanks are due to Mr Kreuger for his participation in the experimental work. We are greatly indebted to Dr C. H. Stam for critical reading of the manuscript.

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## Neutron Diffraction Study of $\text{NH}_4\text{Br}$ and $\text{NH}_4\text{I}$

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$\text{NH}_4\text{Br}$ , which has the caesium-chloride structure, and  $\text{NH}_4\text{I}$ , which has the sodium chloride structure, have been studied by neutron diffraction, mainly to determine the orientation and vibrational behaviour of the  $\text{NH}_4$  groups. For  $\text{NH}_4\text{Br}$ , a model with eight  $\frac{1}{2}$ -hydrogen atoms in  $\langle 111 \rangle$  directions, and isotropic, Gaussian libration of the hydrogen atoms, seemed to provide an adequate description of the diffraction results with physically plausible parameters. For  $\text{NH}_4\text{I}$ , the hydrogen distribution has broad peaks in the six  $\langle 100 \rangle$  directions and unusually large vibration amplitudes for the ions; the most profitable method of refinement was to describe the hydrogen distribution by Kubic Harmonics.

### Introduction

$\text{NH}_4\text{Br}$  has the caesium chloride structure in the temperature range  $-38$  to  $138^\circ\text{C}$ . It is obvious that the  $\text{NH}_4$  tetrahedra must be oriented with N-H bonds in  $\langle 111 \rangle$  directions. Two orientations are possible and it has been established by Levy & Peterson (1953) that there is complete disorder between them.

Above  $138^\circ\text{C}$   $\text{NH}_4\text{Br}$  transforms to the sodium chloride structure but crystals large enough for neutron diffraction break up in the transition. Therefore, to study ammonium halides in the sodium chloride phase, we used crystals of  $\text{NH}_4\text{I}$ , which has this structure above  $-17.6^\circ\text{C}$ . In this structure there is no obvious way in which the tetrahedral  $\text{NH}_4$  ion can fit in with the octahedral symmetry of the  $\text{NH}_4$  site. Several possible models were discussed by Levy & Peterson (1953) but none of them was clearly established.

### Collection and analysis of data on $\text{NH}_4\text{Br}$

A single crystal of  $\text{NH}_4\text{Br}$  was grown from an aqueous solution doped with urea. Its approximate dimensions were  $7 \times 4 \times 2$  mm. Data were collected on a four-circle computer-controlled neutron diffractometer at the Australian Atomic Energy Commission. The instrument has been described by Pryor, Ellis & Dullow (1969).

At room temperature 50 reflexions were measured with a wavelength of  $1.05 \text{ \AA}$ , and 30 at a wavelength of  $1.55 \text{ \AA}$ . The crystal was then mounted in a silica tube packed with alumina wool. A fine heater wire was spiralled inside the tube and supplied from a stabilized d.c. supply. At  $120^\circ\text{C}$ , 50 reflexions were measured at wavelength  $1.05 \text{ \AA}$  and, at  $136^\circ\text{C}$ , 50 reflexions at  $1.17 \text{ \AA}$ . In every case three symmetry-related equivalents of each reflexion were measured.

The observed intensities were corrected for absorption, using an absorption coefficient,  $\mu$ , of  $2.5 \text{ cm}^{-1}$ , with the program *CDRABS* (written by G. W. Cox and M. M. Elcombe, of A.A.E.C.). This program also provides values of the mean path length  $\bar{T} = \int T \exp(-\mu T) dv / \int \exp(-\mu T) dv$ , where  $T$  is the path length in the crystal, which is required for extinction corrections. In these ammonium salts, as in all other hydrogen-containing materials, the true value of the absorption coefficient,  $\mu$ , is not known. However in these refinements, described next, for extinction and structural parameters, no result was altered outside 1 estimated standard deviation by varying  $\mu$  between 2.0 and  $3.0 \text{ cm}^{-1}$ .

The absorption-corrected data were subjected to a preliminary refinement based on the structural model described below. Comparison of the observed and calculated structure factors indicated that the data were

probably affected by extinction. It was assumed that primary extinction was negligible and the single extinction parameter  $r^*$  was added to the refinement program to correct for secondary extinction using the formula (Zachariassen, 1968),

$$|F_0| = |F_{\text{obs}}| \left\{ 1 + \frac{2T\lambda^2 F_{\text{obs}}^2 r^*}{V^2 \sin^2 2\theta} \right\}^{-1/4} \quad (1)$$

where,

$$r^* = r \left( 1 + \frac{r^2}{\lambda^2 g^2} \right)^{1/2},$$

$r$  is the mean radius of a perfect volume of crystal and  $g$  is the mosaic spread parameter. The weights used in these refinements were obtained from the formula  $w = 1/\sigma^2$  where  $\sigma^2 = \sigma_s^2 + 0.03I$ , and  $\sigma_s$  is the standard deviation due to counting statistics alone and  $I$  is the observed intensity. In these refinements the symmetry-related equivalents appear separately but some of them with large errors were rejected. The values of  $r^*$  from these refinements were:

$$\begin{aligned} T = 23^\circ\text{C} \quad \lambda = 1.05 \quad r^* &= 3,400(800) \text{ \AA} \\ &\lambda = 1.55 \quad r^* = 3,500(900) \\ T = 120^\circ\text{C} \quad \lambda = 1.05 \quad r^* &= 2,000(600) \\ T = 136^\circ\text{C} \quad \lambda = 1.17 \quad r^* &= 3,100(1000) . \end{aligned}$$

(Here, and elsewhere in this paper, the figures in brackets are 1 e.s.d. obtained from the least squares refinements.)

The fact that  $r^*$  does not change from wavelength 1.05 to 1.55 Å indicates that the crystal is of type II in the terminology of Zachariassen (1968) and hence the assumption that primary extinction could be neglected is valid.

All observations were then corrected using equation (1) with  $r^* = 3500$  Å. For the 23°C data the scale factors from these initial refinements were also applied and the two sets of data for the two wavelengths were averaged. Finally the symmetry-related equivalents were averaged to give the  $F_0$  values for the final refinements.

In the refinement of structure factors it was assumed that the ammonium group was completely disordered between the two possible orientations. Half-hydrogen atoms were placed in eightfold positions  $c/\sqrt{3}$  ( $\pm 1, \pm 1, \pm 1$ ) where  $c$  is the N-H bond length, and  $N$  is at the origin.

The thermal motions of the Br and N atoms were described by the traditional Debye-Waller factors of the form  $\exp(-B \sin^2 \theta/\lambda^2)$ . The thermal motion of the hydrogen atoms was described as a convolution of three components: the isotropic, Gaussian displacement of the NH<sub>4</sub> group; an isotropic, Gaussian libration about the equilibrium position; and a Gaussian oscillation of the H atom along the N-H bond. That is to say the description of the thermal motion in the refinement was formulated directly in terms of parameters that lend themselves to a physical interpretation.

The angular vibration is described in real space as:

$$t(\sigma) = \exp(-\sigma^2/\langle\sigma^2\rangle)$$

where  $t(\sigma)$  is the probability of an angular displacement of  $\sigma$ , and  $\langle\sigma^2\rangle$  is the mean-square amplitude of angular vibration. The problem of evaluating the Fourier transform of a curvilinear motion like this has been discussed recently by Pryor & Sanger (1970) and leads to the formula:

Table 1. Refinement of the NH<sub>4</sub>Br data

Figures in brackets are estimated standard deviations.

Parameter	23°C	120°C	136°C	23°C (Using conventional Debye-Waller factor)
	$B_N$ B factor of NH <sub>4</sub> group (Å <sup>2</sup> )	2.31 (0.03)	2.62 (0.09)	3.48 (0.06)
$B_{Br}$ B factor of Br, (Å <sup>2</sup> )	2.01 (0.04)	2.56 (0.10)	3.10 (0.06)	2.08 (0.04)
$c$ N-H bond length, (Å)	1.046 (0.005)	1.049 (0.010)	1.040 (0.005)	1.019 (0.005)
$\langle\sigma^2\rangle^{1/2}$ R.m.s. angular vibration of NH <sub>4</sub> group (°)	11.0 (0.5)	12.4 (0.9)	12.1 (0.6)	11.3 (0.5)
$\langle u^2\rangle^{1/2}$ R.m.s. vibration of N-H bond length (Å)	0.10 (0.03)	0.11 (0.05)	0.10 (0.02)	0.11 (0.03)
$R_w$ (%)	3.7	4.0	2.5	4.1
$R_u$ (%)	3.5	4.4	2.7	3.8

Table 2. Comparison of experimental and calculated values of the amplitudes of rotation and bond vibration and experimental values of the Debye diffraction temperature

Figures in brackets are estimated standard deviations.

Temperature	Rotational amplitude $\langle\sigma^2\rangle^{1/2}$		Bond-vibration amplitude $\langle u^2\rangle^{1/2}$		Debye temperature
	Exp.	Calc.	Exp.	Calc.	$\theta_m$
23°C	11.0 (0.5)°	9.4°	0.10 (0.3) Å	0.073 Å	184.1°K
120	12.4 (0.9)	10.1	0.11 (0.05)	0.073	186.8
136	12.1 (0.6)	10.1	0.10 (0.02)	0.073	171.5

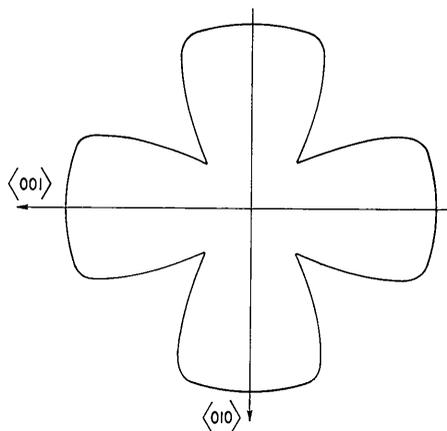


Fig. 1. Angular dependence of the nuclear density of hydrogen atoms on the surface of a sphere of radius equal to the N-H distance of 1.048 Å. The distributions shown are the results of refinements of the NH<sub>4</sub>I data using Cubic Harmonics  $K_0, K_2, K_3$ .

$$T_R = \frac{\exp \left[ -\frac{1}{2} \left\{ \frac{Q^2 c^2 - (\mathbf{Q} \cdot \mathbf{c})^2 \langle \sigma^2 \rangle}{1 - i \mathbf{Q} \cdot \mathbf{c} \langle \sigma^2 \rangle} \right\} \right]}{1 - i \mathbf{Q} \cdot \mathbf{c} \langle \sigma^2 \rangle} \quad (2)$$

where  $\mathbf{Q}$  = the scattering vector (with  $Q = 4\pi \sin \theta / \lambda$ ) and  $\mathbf{c} = c/\sqrt{3}$  ( $\pm 1, \pm 1, \pm 1$ ). When this complete formulation is used there is no longer any need to apply a 'libration correction' (see Cruickshank, 1961) to the bond length.

The bond-vibration part, when Fourier-transformed, becomes

$$T_L = \exp \left\{ -\frac{1}{2} [(\mathbf{Q} \cdot \mathbf{c})^2 \langle u^2 \rangle] \right\}$$

where  $\langle u^2 \rangle$  is the mean-square vibration amplitude along the bond.

The complete formula used in the refinement was:

$$kF_c = T_N [b_N + \frac{1}{2} b_H \sum_c T_R T_L \exp(i\mathbf{Q} \cdot \mathbf{c})] \pm T_B b_{Br}, \quad (3)$$

where  $T_N = \exp(-B_N \sin^2 \theta / \lambda^2)$ ,  $T_{Br} = \exp(-B_{Br} \sin^2 \theta / \lambda^2)$ ,  $B_N$  = the  $B$  factor of the NH<sub>4</sub> group,  $B_{Br}$  = the  $B$  factor of Br, and  $b_N, b_H, b_{Br}$  are the scattering lengths of the N, H and Br atoms respectively, taken from the recent table published by the Neutron Diffraction Commission (1969).

A full-matrix least-mean-squares refinement of the absorption-extinction-corrected data, based on equation (3) gave the parameters of Table 1. The  $R$  indices referred to in the Tables are  $R_w = (\sum w \Delta^2 / \sum w F_o^2)^{1/2}$ ,  $R_u = \sum |\Delta| / \sum |F_o|$ , and  $\chi^2 = \sum w \Delta^2 / (n - p)$  where  $\Delta = |F_o| - |F_c|$ ,  $n$  is the number of reflexions, and  $p$  is the number of parameters.

It is of interest to determine whether the elaborate formula for  $T_R$  [equation (2)] including the effect of curvilinear motion of the H atoms, makes much difference to the refinement. This is easily done by putting  $i\mathbf{Q} \cdot \mathbf{c} \langle \sigma^2 \rangle = 0$  in equation (2). The results of this refinement are given in the fourth column of Table 1 for the 23°C data. The value of the  $R$  indices is slightly in-

Table 3. Refinements of NH<sub>4</sub>I data using various models to describe the NH<sub>4</sub> ion orientation. Figures in brackets are estimated standard deviations.

Model	a	b	c	d	e	f	g	h
$B$ factor of I (Å <sup>2</sup> )	3.8 (0.4)	3.3 (0.3)	3.7 (0.2)	3.7 (0.2)	4.2 (0.5)	4.2 (0.5)	4.5 (0.8)	3.9 (1.1)
$B$ factor of NH <sub>4</sub> ion (Å <sup>2</sup> )	4.2 (0.4)	3.8 (0.3)	4.3 (0.2)	4.3 (0.2)	4.4 (0.4)	4.4 (0.4)	5.6 (0.6)	3.5 (0.8)
N-H bond length	1.05 (0.02)	1.04 (0.01)	1.05 (0.01)	1.05 (0.01)	0.91 (0.10)	0.90 (0.09)	0.94 (0.05)	0.92 (0.14)
R.m.s. angular vibration of NH <sub>4</sub> ion	—	—	7.7 (0.7)	9.3° (0.9)	42.0° (8.0)	42.0° (7.0)	—	—
$R_w$ (%)	13.7	10.0	5.3	5.6	13.6	14.3	22.0	28.0
$R_u$ (%)	12.4	9.0	5.6	5.9	12.6	13.0	21.0	23.0
$\chi^2$	5.0	2.7	0.3	0.9	5.1	5.7	13.0	22.0

creased; none of the vibration parameters are significantly altered, but the N-H bond length is shorter. Note, however, that when Cruickshank's libration correction of  $\frac{1}{2}c\langle\sigma^2\rangle$  ( $=0.020$  Å) is applied the value of column 1 is recovered (within 1 e.s.d.). It may therefore be said that the longer formula is not really necessary.

#### Discussion of NH<sub>4</sub>Br results

The vibration parameters of Table 1 lend themselves to straightforward interpretation. We have  $4\pi^2\nu_R^2 I\langle\sigma^2\rangle = \varepsilon_R$  and  $4\pi^2\nu_L^2 m_H\langle u^2\rangle = \varepsilon_L$  where  $I$  is the moment of inertia of the NH<sub>4</sub> group,  $m_H$  the mass of an H atom,  $\varepsilon_R$  and  $\varepsilon_L$  are the energies of rotational oscillation and of bond-length oscillation. The frequency of rotational oscillation,  $\nu_R$ , is quoted by Venkataraman, Usha, Iyengar, Vijayaraghavan & Roy (1962) and that of bond length oscillation,  $\nu_L$ , by Herzberg (1951), as 298 cm<sup>-1</sup> and 3350 cm<sup>-1</sup> respectively. Energies are calculated from the usual formula,  $\varepsilon = h\nu/2 + nh\nu$  with  $n = \{\exp(-h\nu/kT) - 1\}^{-1}$ . The comparison of experimental and calculated values is shown in Table 2 and is quite satisfactory.

The  $B$  factors are not susceptible to such a straightforward interpretation. However, as the transition temperature is approached, they seem to increase faster than the usual formulae would predict. To illustrate this we have calculated the conventional Debye temperature,  $\Theta_m$ , for a diatomic molecule from a well-known formula

$$\frac{1}{2}(m_1 B_1 + m_2 B_2) = \frac{6h^2 T}{k\Theta_m^2} \psi(\Theta_m/T).$$

If the increase in  $B$  factors with temperature is greater than normal then the value of  $\Theta$  will drop. These values are also shown in Table 2 and support our contention of an anomalous increase in vibration amplitude. The value of  $\Theta_m$  calculated at 136°C is about 7% lower than the values calculated at 23 and 120°C, indicating that the experimental  $B$  factors are 14% higher than would be expected.

The N-H bond length, 1.046 (0.005) Å, is slightly larger than the value 1.031 (0.004) Å obtained by Gutowsky, Pake & Bersohn (1954) from nuclear magnetic resonance.

#### Collection and analysis of NH<sub>4</sub>I data

With the single crystal of NH<sub>4</sub>I the intensities of 42 reflexions were measured with a neutron wavelength of 1.17 Å and the intensities of 80 reflexions were measured at a wavelength of 1.55 Å. At both wavelengths measurements were taken on three symmetry-related equivalents of each reflexion. The dimensions of the crystal were about 2 × 2 × 1 mm. For this crystal the absorption correction is negligible and, if we assume the extinction parameter  $r^*$  is of the same order as determined for NH<sub>4</sub>Br, extinction is also small. It could not be determined from the experiment.

The intensities of the symmetry-related equivalents were averaged. The two sets of data at the two wavelengths were also averaged after adjustment by the scale factors obtained in preliminary separate refinements.

The first analyses of the data were based on the models discussed by Levy & Peterson (1953). These models propose various orientations of the NH<sub>4</sub> ion as follows:

- free rotation of the NH<sub>4</sub> ion;
- the N-H bond in a  $\langle 100 \rangle$  direction and free rotation of the ion about the bond;
- two hydrogen atoms make closest approaches to two I ions with typical hydrogen positions  $c/\sqrt{6}$  ( $1 - \sqrt{2}$ ,  $1 + \sqrt{2}$ , 0),  $c/\sqrt{6}$  ( $1 + \sqrt{2}$ ,  $1 - \sqrt{2}$ , 0),  $c/\sqrt{6}$  ( $-1$ ,  $-1$ , 2) and  $c/\sqrt{6}$  ( $-1$ ,  $-1$ ,  $-2$ );
- the approach of three hydrogen atoms to three I ions is minimized with hydrogen positions  $c/\sqrt{3}$  ( $-1$ ,  $-1$ ,  $-1$ ),  $c/3\sqrt{3}$  ( $-1$ ,  $-1$ , 5),  $c/3\sqrt{3}$  ( $-1$ , 5,  $-1$ ) and  $c/3\sqrt{3}$  (5,  $-1$ ,  $-1$ );
- the hydrogen atoms have equilibrium positions in  $\langle 100 \rangle$  type planes with typical hydrogen positions  $c/\sqrt{3}$  ( $\sqrt{2}$ , 1, 0),  $c/\sqrt{3}$  ( $-\sqrt{2}$ , 1, 0),  $c/\sqrt{3}$  (0,  $-1$ ,  $\sqrt{2}$ ) and  $c/\sqrt{3}$  (0,  $-1$ ,  $\sqrt{2}$ );
- the hydrogen atoms lie in  $\langle 111 \rangle$  directions;
- the NH<sub>4</sub> ion rotates about its 3-axis which is set parallel to a crystal 3-axis;
- the ion rotates about its 4-axis set parallel to a crystal 4-axis.

In all cases it is assumed that all symmetry-related orientations are occupied with equal probability. In those models ( $c$ ,  $d$ ,  $e$  and  $f$ ) where no rotation of the group

Table 4. Refinements of NH<sub>4</sub>I data using Cubic Harmonics to describe the hydrogen distribution

Figures in brackets are estimated standard deviations.

	Kubic harmonics	$K_0$	$K_0, K_2$	$K_0, K_2, K_3$	$K_0, K_2, K_3, K$	$K_0, K_2, K_3, K_{4,5}$
$B_I$	$B$ factor of I (Å <sup>2</sup> )	3.8 (0.4)	3.63 (0.10)	3.64 (0.10)	3.64 (0.10)	3.63 (0.10)
$B_{NH_4}$	$B$ factor of NH <sub>4</sub> ion (Å <sup>2</sup> )	4.2 (0.4)	4.27 (0.10)	4.29 (0.10)	4.29 (0.10)	4.27 (0.10)
$c$	N-H bond length (Å)	1.05 (0.02)	1.052 (0.001)	1.053 (0.006)	1.053 (0.006)	1.054 (0.006)
	$a_2$		4.0 (0.2)	4.1 (0.2)	4.1 (0.2)	4.1 (0.2)
	$a_3$			-31.2 (10.0)	-31.2 (10.4)	-31.7 (10.5)
	$a_4$				0.61 (21.0)	3.8 (21.0)
	$a_4$					-430.0 (650.0)
	$R_w$ (%)	13.7	4.15	3.67	3.70	3.65
	$R_u$ (%)	12.4	3.9	4.0	4.0	3.9
	$\chi^2$	5.0	0.5	0.4	0.4	0.4

is involved, the  $\text{NH}_4$  ion can librate about its equilibrium position. The Fourier transform of the smearing function of a hydrogen atom undergoing such libration is given by equation (2). The structure factors were calculated using the expression

$$k|F_c| = T_N(b_N + b_H T_H) \pm T_I b_I, \quad (4)$$

where the  $b$  values are the neutron scattering lengths,  $T_N = \exp(-B_N \sin^2 \theta / \lambda^2)$ ,  $T_I = \exp(-B_I \sin^2 \theta / \lambda^2)$  and  $T_H$  is the Fourier transform of the distribution of hydrogen density given by one of the above models. The results of refinements of the  $\text{NH}_4\text{I}$  data using each of the models are given in Table 3.

A general way, independent of any physical model, of describing the  $\text{NH}_4$  ion orientation is to describe the distribution of nuclear density of the hydrogen atoms around the central nitrogen atom in terms of Cubic Harmonic functions (von der Lage & Bethe, 1947). The distribution of the four hydrogen atoms in real space, with the N atom at rest, can be written:

$$t_H(\mathbf{r}) = \frac{1}{\pi c^2} \sum a_m K_m \delta(r - c), \quad (5)$$

where  $\delta$  is the Kronecker delta function, the  $a_m$  are amplitude coefficients, and the  $K_m$  are angle-dependent functions, the centrosymmetric Cubic Harmonics.

The first few  $K_m$  are:

$$\begin{aligned} K_0 &= 1, \quad K_1 = 0, \quad K_2 = (x^4 + y^4 + z^4)/\rho^4 - 3/5, \\ K_3 &= x^2 y^2 z^2 / \rho^6 + K_2 / 22 - 1/105, \\ K_4 &= (x^8 + y^8 + z^8) / \rho^8 - 28K_3 / 5 - 210K_2 / 143 - 1/3, \end{aligned}$$

where  $\rho^2 = x^2 + y^2 + z^2$ . To calculate the structure factors the Fourier transforms of the Cubic Harmonics as given by Sanger (1968) were used.

The total hydrogen distribution in real space is a convolution of the  $t_H(\mathbf{r})$  with the thermal smearing function of the  $\text{NH}_4$  group so that the structure factors are given by the expression (4) where  $T_H$  is the Fourier transform of  $t_H(\mathbf{r})$ . The  $|F_c|$  were fitted to the data by the least-squares method with the coefficients,  $a_m$ , as parameters (but with  $a_0$  held fixed at 1 in order to provide correct normalization). These refinements are given in Table 4.

It is obvious that the Cubic Harmonic description is significantly better than the best of the models, and that the two coefficients  $a_2$  and  $a_3$  are enough: nothing is gained by adding further coefficients. The angular distribution of hydrogen atoms, calculated from equation (5) with  $a_0 = 1$ ,  $a_2 = 4.1$ ,  $a_3 = 31.2$ , is shown in Fig. 1.

#### Discussion of $\text{NH}_4\text{I}$ results

The refinements using Cubic Harmonics converged to a better  $R$  index than any of the models and show the hydrogen atoms smeared out in sixfold positions with a full width at half maximum height of about  $70^\circ$ . A weakness of all the models proposed by Levy & Peterson is that they assume the N atom remains in the

face-centred position. It is probable that the N atom undergoes a displacement so that the tetrahedral  $\text{NH}_4$  ion can attain an equilibrium position in the field of the six surrounding I ions. For example, a displacement of about  $0.1 \text{ \AA}$  in  $\langle 110 \rangle$  directions allows the hydrogen atoms of model (c) – closest approach by two hydrogen atoms to two I ions – to fall within the distribution of Fig. 1. The observed  $B$  factors are much larger than what might reasonably be expected. For a diatomic lattice,  $B$  values can be calculated by the well-established technique (Pryor, 1966) of solving the secular equation for a mesh of points in the Brillouin zone. This was done, over a mesh of 64,000 points, for a simple rigid-ion model, the parameters of which were obtained from the compressibility of  $6.6 \times 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$  for  $\text{NH}_4\text{I}$  in the NaCl phase (Gibbs & Jarman, 1962), and gave values of  $2.04$  and  $1.99 \text{ \AA}^2$  for the  $B$  factors of the  $\text{NH}_4$  and I ions respectively, compared with the experimental values of  $4.26$  and  $3.69 \text{ \AA}^2$ . This discrepancy suggests that there are displacements of both ions away from their face-centred positions.

The analysis also illustrates the value of Cubic Harmonics in some situations involving cubic symmetry. They do not always provide the best approach however. If the  $\text{NH}_4\text{Br}$  results were analysed using Cubic Harmonics the description was still inadequate even with Harmonics up to  $K_8$ : the peaks in the angular distribution are too sharp for a convenient description in terms of Cubic Harmonics. It is essential to be sure that the sum is taken to as many terms as are necessary.

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