Short-Range Order in ND₄Br Studied by Diffuse Neutron Scattering

By R. S. Seymour

School of Physics, University of New South Wales, Kensington, New South Wales 2033, Australia

Diffuse elastic scattering of neutrons has been observed from a single crystal of deuterated ammonium bromide and is interpreted as being due to short-range order among ammonium ion orientations. Both the temperature dependence of the diffuse intensity and its distribution in reciprocal space can be described in terms of a simple Ising model of the order–disorder transition. An expression for the diffuse intensity obtained from the mean-field approximation to the Ising model is least-squares fitted to the data. Interactions between first, second and third nearest neighbour ammonium ions have to be included in the model to give an adequate fit. The interaction energies so obtained are compared with calculations based on a simple electrostatic theory. For agreement, a charge of $0.358e$ on hydrogen atoms and a polarizability of 1.40 Å³ for Br⁻ ions have to be assumed in the calculations and the significance of these unlikely values is discussed.

Introduction

The ammonium halides undergo a number of phase transitions in their solid state with varying temperature and pressure [see Stevenson (1961)]. Among these are the second order transitions which involve a change from order to disorder in the ammonium ion orientations with increasing temperature. It has been established by the neutron diffraction experiments of Levy & Peterson (1952, 1953) that ammonium chloride and ammonium bromide (and the deuterated salts) at room temperature, belong to the space group $Pm3m$ (no. 221 in *International Tables for X-ray Crystallography*, 1952) with the anion at position 1(*b*) and the nitrogen atom at 1(*a*). The ammonium ion can have two possible orientations (designated + and − in this paper) and there is disorder among these so that the hydrogen atoms occupy at random the positions 8(*g*) with an average site occupancy of ½; $x = 0.1488$ for NH₄Br at 23°C (Seymour & Pryor, 1970). As the temperature is lowered the salts change to the ordered states. The space groups of NH₄Cl and ND₄Cl become $P\bar{4}3m$ (no. 215) and the ammonium ions are ordered parallel with the hydrogen atoms in 4(*e*) positions (Levy & Peterson, 1952). The structures of NH₄Br and ND₄Br, however, become tetragonal [space group $P4/nmm$ (no. 129)] below the transition temperature (Ketelaar, 1934; Weigle & Saini, 1936) with the ammonium ions ordered parallel along the tetragonal *c* axis but ordered anti-parallel in *a–b* planes (Levy & Peterson, 1953). The tetragonal structure is a slight distortion of the cubic structure with the *c* axis extended by only about 0.3% with respect to the *a* and *b* axes. In addition the Br⁻ ions are displaced along the tetragonal axis with neighbouring rows alternatively displaced positively or negatively relative to the *a–b* plane. At a lower temperature still, NH₄Br and ND₄Br transform to the $P\bar{4}3m$ structure.

These transitions have been described with an Ising model by Nagamiya (1942, 1943). Most Ising model systems exhibit some short-range order in the disordered state and Levy & Peterson noticed diffuse scattering of neutrons from powder samples of ND₄Cl and ND₄Br indicating the existence of such short range order in these substances.

The purpose of the present investigation was to study the temperature dependence of the diffuse scattering of neutrons from a single crystal of ND₄Br and also the distribution of scattered intensity in reciprocal space. From such a study conclusions about the applicability of the Ising model description can be made. The ordering in the ammonium salts involves only hydrogen positions and is most conveniently studied by neutron diffraction. The deuterated salt was used because the large incoherent background from the hydrogenous salt would have made the diffuse scattering difficult to observe. The bromide was chosen rather than the chloride because the anti-parallel ordering in ND₄Br was expected to give diffuse scattering centred away from the reciprocal-lattice points while the diffuse scattering from ND₄Cl would be centred at the reciprocal-lattice points and would be more difficult to measure because of the presence of the Bragg peak. The reciprocal super-lattice points for the ordered state of ND₄Br occur at $(\frac{1}{2} + h, \frac{1}{2} + k, l)$ positions and the diffuse scattering from the disordered phase was expected to be centred at these positions.

Elastic diffuse scattering from ND₄Br

The diffuse scattering from ND₄Br in the disordered phase is due mainly to the short-range order of ND₄⁺ ion orientations, though there is also a small contribution from the displacements of the Br⁻ ions. Considering only the scattering from the ND₄⁺ ions, the diffuse scattering per unit cell is given by

$$I(\mathbf{Q}) = |\varDelta(\mathbf{Q})|^2 \langle |\sigma_{\mathbf{q}}|^2 \rangle \qquad (1)$$

where $\varDelta(\mathbf{Q})$ is half the difference in structure factor for neutron scattering from a ND_4^+ ion in the + and − orientations. For isotropic Debye–Waller factors for the deuterium atoms $\varDelta(\mathbf{Q})$ can be written

$$\varDelta(\mathbf{Q}) = i4b_d \ \sin \frac{Q_1 c}{\sqrt{3}} \sin \frac{Q_2 c}{\sqrt{3}} \sin \frac{Q_3 c}{\sqrt{3}} \exp \left(\frac{-B|\mathbf{Q}|^2}{16\pi^2} \right) \qquad (2)$$

where $\mathbf{Q} = (Q_1, Q_2, Q_3)$ is the scattering vector, ($|\mathbf{Q}| = 4\pi \sin \theta/\lambda$), b_d is the neutron scattering length for deuterium, c is the nitrogen-deuterium bond length, and B is the isotropic temperature factor for a deuterium atom.

The $\langle |\sigma_{\mathbf{q}}|^2 \rangle$ in expression (1) is the Fourier transform of an ensemble average of correlations between orientations of ND_4^+ ions on different lattice sites. It can be related to the Fourier transform, $v(\mathbf{q})$ of the interaction energies of neighbouring ND_4^+ ions by

$$\langle |\sigma_{\mathbf{q}}|^2 \rangle = [1 + \beta v(\mathbf{q})]^{-1} \qquad (3)$$

where $\beta = (kT)^{-1}$, k is Boltzmann's constant and T is temperature. The expression (3) is derived from the mean-field approximation to the Ising model (Brout, 1965; Clapp & Moss, 1966; $v(\mathbf{q})$ is given by

$$v(\mathbf{q}) = \sum_j{}' v_{jk} \exp \{i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)\} \qquad (4)$$

where the $j = k$ term is excluded in the summation over all ND_4^+ ion sites, $\mathbf{q}$ is a vector in the first Brillouin zone, and $\mathbf{R}_j$ are the position vectors of the nitrogen atoms. The interactions v_{jk} are

$$v_{jk} = \tfrac{1}{4}(V_{jk}^{++} + V_{jk}^{--} - V_{jk}^{-+} - V_{jk}^{+-}) \qquad (5)$$

with V_{jk}^{++} the energy of interaction between and ND_4^+ ion on the site j in the lattice in the + orientation and

an ND_4^+ ion on site k in the + orientation, with V_{jk}^{--}, V_{jk}^{-+}, V_{jk}^{+-} defined similarly. For the ammonium chloride and bromide systems, V_{jk}^{++} and V_{jk}^{--} are equal.

The distribution of diffuse intensity within a Brillouin zone is mainly determined by the $\mathbf{q}$ dependence of the $\langle |\sigma_{\mathbf{q}}|^2 \rangle$ and equation (3) shows that the maximum in $\langle |\sigma_{\mathbf{q}}|^2 \rangle$ occurs at position $\mathbf{q}$ in each Brillouin zone where $v(\mathbf{q})$ is a minimum. It is therefore of interest to determine the positions of the minima of $v(\mathbf{q})$ for various values of the v_{jk}. This has been done by Clapp & Moss (1968) for the body-centred and face-centred cubic alloys. In ammonium bromide and chloride the ammonium ions form a simple cubic lattice and $v(\mathbf{q})$ can be written

$$v(\mathbf{q}) = 2v_{01} \{\cos (q_1 a) + \cos (q_2 a) + \cos (q_3 a)\}$$
$$+ 4v_{02} \{\cos (q_1 a) \cos (q_2 a) + \cos (q_2 a) \cos (q_3 a)$$
$$+ \cos (q_3 a) \cos (q_1 a)\}$$
$$+ 8v_{03} \cos (q_1 a) \cos (q_2 a) \cos (q_3 a) \qquad (6)$$

where a is the lattice constant, v_{01} is the interaction energy between ions that are nearest neighbours in $\langle 100 \rangle$ directions, v_{02} in $\langle 110 \rangle$ directions and v_{03} in $\langle 111 \rangle$ directions. Interactions between more distant neighbours have been neglected.

The q_i take values between $-\pi/a$ and $+\pi/a$; however, this range can be restricted to $0 \le q_i \le \pi/a$, because of the symmetry of $v(\mathbf{q})$, so that if a minimum in $v(\mathbf{q})$ occurs at $\mathbf{q}_m$ there is also a minimum at all symmetry-related equivalents of $\mathbf{q}_m$. Differentiation of (6) shows that extrema occur at: (000); $2\pi/a$ ($\tfrac{1}{2}\tfrac{1}{2}0$); $2\pi/a$ ($\tfrac{1}{2}00$); $2\pi/a$ ($\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$). Fig. 1 shows where the minima occur for various values of the ratios a_{02}/v_{01} and v_{03}/v_{01}.

Experimental

A single crystal ($10 \times 10 \times 5$ mm) was used in the experiment. The crystal was grown by slow cooling of a solution of equal parts of ND_4Br and deuterated urea in heavy water. The urea is necessary to make the ND_4Br grow in a cubic habit. The deuteration of the ammonium bromide and urea was accomplished by dissolving equal parts of the normal materials together in 99·8% D_2O, recovering the crystals by distillation under vacuum and then repeating the procedure four times.

The crystal was mounted with a [110] axis vertical on a liquid nitrogen cryostat and the measurements were carried out with the 6H1 triple-axis spectrometer of the Australian Atomic Energy Commission. All measurements were made with the analyser of the triple-axis instrument set to receive elastically scattered neutrons only.

Results

A preliminary survey of the (110) zone made at room temperature indicated some diffuse scattering centred at the reciprocal-lattice points 1·5, 1·5, 1·0 and 2·5,
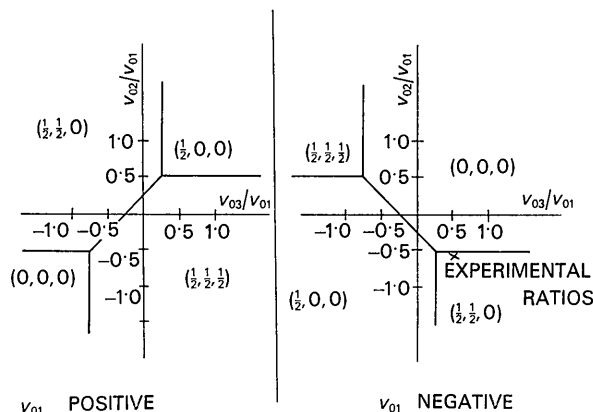

Fig. 1. Diagrams showing the ranges of the ratios v_{03}/v_{01} and v_{02}/v_{01} for the simple cubic Ising system that would give diffuse intensity maxima at the reciprocal-space positions indicated. The point corresponding to the experimental ratios for ND_4Br is shown.

2·5, 1·0. There was no diffuse scattering around the Bragg peaks. The temperature was lowered to −47 °C (11 °C above the reported transition temperature) and it was observed that the diffuse peaks at 1·5, 1·5, 1·0 and 2·5, 2·5, 1·0 were much more intense and weak diffuse peaks were noticed at 0·5, 0·5, 1·0 and 2·5, 2·5, 2·0.

All the diffuse peaks showed strong temperature dependence as is shown for the 1·5, 1·5, 1·0 peak in Fig. 2. The intensity contours in the (110) zone were similar for all the peaks and retained their basic shape at all temperatures. The intensity contours around the 1·5, 1·5, 1·0 peak are shown in Fig. 3.

Temperature-dependence of diffuse scattering

Equations (1) and (3) predict that a plot of inverse diffuse intensity against inverse temperature should give a straight line. Fig. 4 shows the experimental results plotted in this way for various q around the point 1·5, 1·5, 1·0. A background had to be subtracted from the experimental intensities to give the straight lines obtained. This background was estimated from the data at 1·5, 1·5, 1·0 as being that which was necessary to give the straight line. Extrapolation of the 1·5, 1·5, 1·0 data to the T^{-1} axis gave a value of $215·5 \pm 2·0\,°K$ for the transition temperature compared with a reported value for ND₄Br of $214·6\,°K$ (Stephenson & Adams, 1952). The error quoted for extrapolated transition temperature is a least-squares estimated standard deviation. Observations were weighted in accordance with the usual expression for counting statistics, $w = (I + 2B)^{-1}$.

Q-dependence of diffuse scattering

The maxima in diffuse intensity occur at positions $q = 2\pi/a(\frac{1}{2}\frac{1}{2}0)$ plus a reciprocal-lattice vector and the variation in intensity of the diffuse peaks from one Brillouin zone to the next can be explained by the Q-dependence of the structure factor $|A(Q)|^2$ as given in equation (2).

The variation of diffuse intensity within a Brillouin zone depends on the interaction energies v_{0i} through equations (4), (3) and (1). A least-squares fit of intensity calculated with these equations was therefore made to the experimental data at $-52·5\,°C$ around the point 1·5, 1·5, 1·0 with the v_{0i} and a scale factor as parameters. The data consisted of readings taken over a mesh containing 287 points and covering the region in the (110) zone of reciprocal space, bounded by the lines $(x, x, 1·06]$, $[x, x, 0·94]$, $[1·25, 1·25, x]$, $[1·75, 1·75, x]$, and an additional 100 readings taken from separate scans along the lines $[1·0, 1·0, x]$, $[2·0, 2·0, x]$, $[x, x, 1·5]$, $[x, x, 0·5]$, $[x, x, 1·0]$ and $[1·5, 1·5, x]$. The intensities were first corrected for incoherent background using the value of the background found from the analysis of the temperature-dependence of the data. Also weights of $w = (I_o + 2B)^{-1}$ were alloted to each measure-

ment, where I_o is the measured diffuse intensity and B is the estimated background.

The results are shown in Table 1 where the figures in brackets are least-squares estimated standard deviations. The R values referred to are

$$R_w = (\textstyle\sum w \, \Delta^2 / \sum w I_o^2)^{1/2}, \quad R_u = \sum |\Delta| / \sum I_o,$$

and $\chi^2 = \sum w \Delta^2/(n-p)$, where $\Delta = I_o - I_c$, I_o is the observed (background corrected) intensity, I_c is calculated from equation (1), n is the number of data and p is the number of parameters.

An adequate fit to the data was obtained with interactions out to and including third nearest neighbours.
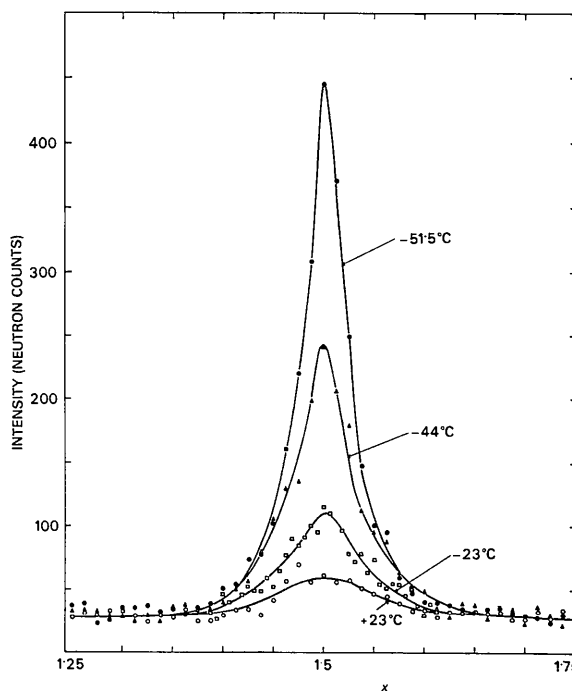

Fig. 2. Scans along the line $[x, x, 1·0]$ in reciprocal space showing the diffuse scattering from ND₄Br at various temperatures.
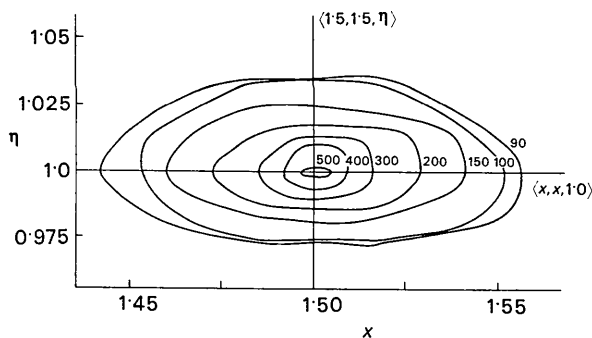

Fig. 3. Diffuse intensity contour from ND₄Br at $-52·5\,°C$ in the (110) zone of reciprocal space around the point 1·5, 1·5, 1·0. The intensities are neutron counts.

Table 1 shows that inclusion of fourth nearest neighbour interactions gave no improvement. An estimate of the diffuse scattering expected from the small displacements of the two ions showed that its intensity would be less than 5% of that due to the short-range order of the ND_4^+ ion orientations and was neglected in the refinements.

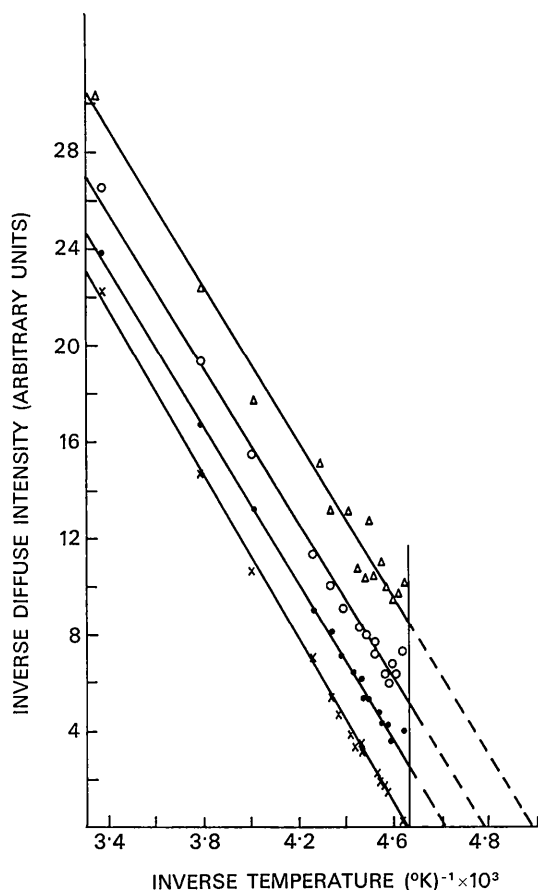Fig. 4. Plots of inverse diffuse intensity (background corrected) against inverse temperature at the reciprocal space positions: $x - 1\cdot5$, $1\cdot5$, $1\cdot0$; $\bullet - 1\cdot475$, $1\cdot475$, $1\cdot0$; $\bigcirc - 1\cdot462$, $1\cdot462$, $1\cdot0$; $\triangle - 1\cdot45$, $1\cdot45$, $1\cdot0$.

Calculations of interaction energies

The contribution to the v_{ij} in equation (4) of the electrostatic octupole moment interactions between ammonium ions can be easily calculated by supposing the ammonium ion is a tetrahedron with the hydrogens at the four vertices with electric charge $+\delta e$ and the nitrogen at the centre with charge $(1-4\delta)e$. For ND_4Br with a N–D distance of $1\cdot04$ Å and lattice spacing $4\cdot047$ Å (measured at $220\,°K$) the v_{01}, v_{02}, v_{03}, and v_{04} (divided by Boltzmann's constant)are:

$$
\begin{aligned}
v_{01} &= -609\cdot21\ \delta^2 \\
v_{02} &= 91\cdot02\ \delta^2 \\
v_{03} &= -24\cdot21\ \delta^2 \\
v_{04} &= -4\cdot94\ \delta^2 .
\end{aligned}
\tag{7}
$$

The values obtained with $\delta = 0\cdot25$ are given in Table 1 for comparison with the experimental results. The calculated ratios $v_{02}/v_{01} = -0\cdot15$ and $v_{03}/v_{01} = 0\cdot04$ would give diffuse maxima at $\mathbf{q} = (000)$ positions (see Fig. 1 and neglecting more distant interactions) whereas the experimental diffuse maxima are at $\mathbf{q} = 2\pi/a(\frac{1}{2}\frac{1}{2}0)$.

Better agreement with the experimental results can be obtained by including in the calculations an additional contribution $(v_{ij})_d$, to the v_{ij}, which is due to the interaction of the ammonium ion on site i with the dipoles induced on Br^- ions by the electric field of the ammonium ion on site j. In the completely disordered state the average dipole moment on the Br^- ion is zero. Let $\mathbf{p}_{ki}^+$ be the average dipole moment on the Br^- ion at site k when the ND_4^+ ion on site i is in the $+$ orientation and the rest of the lattice is averaged. If $\mathbf{p}_{ki}^-$ is similarly defined then the $(v_{ij})_d$ can be written:

$$
(v_{ij})_d = \sum_k (\mathbf{p}_{ki} \cdot \mathbf{E}_{kj} + \mathbf{p}_{kj} \cdot \mathbf{E}_{ki})
\tag{8}
$$

where $\mathbf{p}_{ki} = \frac{1}{2}(\mathbf{p}_{ki}^+ - \mathbf{p}_{ki}^-)$ and $\mathbf{E}_{ki}$ is half the difference in electric fields at the Br^- ion site k from the two orientations of the ammonium ion at site i. If α is the isotropic polarizability of the Br^- ion then $\mathbf{p}_{ki} = \alpha\mathbf{E}_{ki}$. Calculations of the $(v_{ij})_d$ were carried out for ND_4Br using equation (8) but restricting the summation over all Br^-

Table 1. *Refinement of data and calculations*

The first two columns show the results of refinements of the diffuse data in the (110) zone around the point $1\cdot5$, $1\cdot5$, $1\cdot0$ and the figures in brackets are standard deviations estimated from the least-squares analysis. The remaining columns give the results of calculations of the interaction energies in ND_4Br from electrostatic considerations with various values of the charge, δ, on the deuterium atoms and the polarizability, α, of the Br^- ions.

	Refinement of data	Refinement of data	Calculation $\delta = 0\cdot25$ $\alpha = 0\cdot0$ Å^3	Calculation $\delta = 0\cdot25$ $\alpha = 4\cdot18$ Å^3	Calculation $\delta = 0\cdot359$ $\alpha = 1\cdot40$ Å^3
v_{01}	$-51\cdot2$ ($0\cdot2$)	$-51\cdot0$ ($0\cdot2$)	$-38\cdot08$	$3\cdot62$	$-49\cdot58$
v_{02}	$29\cdot8$ ($0\cdot1$)	$29\cdot7$ ($0\cdot1$)	$5\cdot69$	$28\cdot34$	$27\cdot37$
v_{03}	$-25\cdot02$ ($0\cdot05$)	$-25\cdot04$ ($0\cdot05$)	$-1\cdot51$	$-34\cdot56$	$-25\cdot96$
v_{04}		$0\cdot3$ ($1\cdot0$)	$-0\cdot31$	$-2\cdot59$	$-2\cdot21$
χ^2	$1\cdot8$	$1\cdot8$			
R_u	$0\cdot18$	$0\cdot18$			
R_w	$0\cdot21$	$0\cdot21$			

ions by the assumption that a dipole moment on a Br$^-$ ion is induced only by nearest neighbour ND$_4^+$ ions. The results were:

$$
\begin{aligned}
(v_{01})_d &= 159\cdot61\ \delta^2\alpha \\
(v_{02})_d &= 86\cdot70\ \delta^2\alpha \\
(v_{03})_d &= -126\cdot51\ \delta^2\alpha \\
(v_{04})_d &= -8\cdot74\ \delta^2\alpha
\end{aligned}
\tag{9}
$$

where the $(v_{0i})_d$ are the energies of interaction divided by Boltzmann's constant and will be in °K if the polarizability α is in Å^3. The total interactions are obtained by adding equations (7) and (9). Other contributions to the v_{ij} that have been neglected here include the interaction of higher order multipoles induced on the Br$^-$ ions with the ND$_4^+$ ions and also the dipole–dipole interaction between neighbouring Br$^-$ ions.

Values of polarizability of halide ions in alkali halide crystals have been determined from refractive index measurements and for the Br$^-$ ion a value of $\alpha = 4\cdot18$ Å^3 has been obtained (see Born & Huang, 1954). The interaction energies were calculated with this α and a $\delta = 0\cdot25$ and the results (shown in Table 1) were again markedly different from the experimental values. However, values of $\alpha = 1\cdot40$ Å^3 and $\delta = 0\cdot358$ are found to give reasonable agreement with experimental results (see Table 1). The value of α was determined by ratios of interaction energies and $\alpha = 1\cdot40$ Å^3 is the mean of two values found by equating experimental with calculated results for both v_{03}/v_{01} (gave $\alpha = 1\cdot35$ Å^3) and v_{02}/v_{01} (gave $\alpha = 1\cdot45$ Å^3). The value of δ determines the magnitude of calculated interaction energies and was choosen to make the transition temperature [which is given by $(2v_{01} + 4v_{02} - 8v_{03})$] the same for calculation and experiment.

Discussion

Both the temperature-dependence and q-dependence of the diffuse scattering have been described by the mean-field approximation to the Ising model and calculations of the interaction energies from simple electrostatic considerations can be made to agree with the experimental results. However the polarizability of the Br$^-$ ions needed in the calculations to reproduce the observed ratios of the interaction energies is $1\cdot40$ Å^3 whereas the value in alkali bromide crystals is $4\cdot18$ Å^3. A calculation of the interaction energies for NH$_4$Cl showed that the polarizability of the Cl$^-$ ions would have to be less than $1\cdot09$ Å^3 to give the expected diffuse peaks at $q = (000)$ positions but the value in alkali chloride crystals is $3\cdot05$ Å^3. The polarizability of the halide ion used in the present calculations is the polarizability along a hydrogen bond direction and also would contain the effect of displacements of the halide ion. It could conceivably be very different from the value obtained from refractive index measurements on alkali halide crystals. Nagamiya (1943) required

values of $2\cdot0$ and $1\cdot5$ Å^3 for the polarizabilities along [100] directions for Br$^-$ and Cl$^-$ ions respectively to account for the stabilities of the ordered phases of NH$_4$Br and NH$_4$Cl.

A consequence of the influence of the hydrogen bond on the polarizability of the halide ion is that the polarizability would be dependent on the distance between hydrogen and halide ions. This dependence could be important in a description of the phase change from ordered anti-parallel to ordered parallel which occurs in ND$_4$Br when the temperature is lowered to 169 °K. The polarizability of the Br$^-$ ion could decrease with temperature because of the lattice contraction and the ratio of interaction energies could become such, that the ordered parallel phase would be more stable than the ordered anti-parallel phase. The experimental ratios of the interaction energies are indicated by the point marked in Fig. 1. This point lies close to the dividing line between the two regions where diffuse peaks occur at $q = 2\pi/a(\frac{1}{2}\frac{1}{2}0)$ and where they would occur at $q = (000)$. A slightly smaller polarizability (e.g. $1\cdot20$ Å^3) for the Br$^-$ ion would give calculated interaction energies with ratios that would give $q = (000)$ diffuse peaks and hence the ordered phase would be ordered parallel (see Clapp & Moss, 1968).

The electric charges on the deuterium atoms had to be adjusted to give the calculated interaction energies the same magnitudes as the experimental results. A charge of $0\cdot358e$ was required here whereas a value of $0\cdot315e$ was deduced from electron diffraction experiments on NH$_4$Cl (Kuwabara, 1959) and $0\cdot18e$ was suggested by Pauling (1960). Clapp & Moss (1968) examined the accuracy of equation (3) derived from the mean-field approximation to the Ising model and stated that the use of this equation in fitting diffuse scattering data would lead to unreliable magnitudes for interaction energies but would give reliable ratios of the energies. The large value of the charge on deuterium atoms obtained here could indicate the inadequacy of the mean-field approximation for the ND$_4$Br system. Also the Ising model itself is perhaps oversimplified in that tunnelling motion of the ND$_4^+$ ion between the two equivalent positions has been neglected as has coupling of the tunnelling and lattice modes. These effects are important in explaining the large differences in transition temperatures of deuterated and hydrogenous KDP (Kobayashi, 1968). The transition temperature of NH$_4$Br is 20 °K higher than for ND$_4$Br and since such a change cannot be accounted for by the simple Ising model it seems that tunnelling motion and its coupling with lattice modes should be included in the description of the transitions.

References

BORN, M. & HUANG, K. (1954). *Dynamical Theory of Crystal Lattices.* p. 107. London: Oxford Univ. Press.
BROUT, R. (1965). *Phase Transitions.* New York: Benjamin.
CLAPP, P. C. & MOSS, S. C. (1966). *Phys. Rev.* **142**, 418.
CLAPP, P. C. & MOSS, S. C. (1968). *Phys. Rev.* **171**, 754.
International Tables for X-ray Crystallography. (1952). Vol. I. Birmingham: Kynoch Press.
KETELAAR, J. A. A. (1934). *Nature, Lond.* **134**, 250.
KOBAYASHI, K. K. (1968). *J. Phys. Soc. Japan,* **24**, 497.
KUWABARA, S. (1959). *J. Phys. Soc. Japan,* **14**, 1205.
LEVY, H. A. & PETERSON, S. W. (1952). *Phys. Rev.* **86**, 766.

LEVY, H. A. & PETERSON, S. W. (1953). *J. Amer. Chem. Soc.* **75**, 1536.
NAGAMIYA, T. (1942). *Proc. Phys. Math. Soc. Japan,* **24**, 137.
NAGAMIYA, T. (1943). *Proc. Phys Math. Soc. Japan,* **25**, 572.
PAULING, L. (1960). *The Nature of the Chemical Bond,* p. 102. New York: Cornell Univ. Press.
SEYMOUR, R. S. & PRYOR, A. W. (1970). *Acta Cryst.* **B26**, 1487.
STEPHENSON, C. C. & ADAMS, H. E. (1952). *J. Chem. Phys.* **20**, 1658.
STEVENSON, R. (1961). *J. Chem. Phys.* **34**, 1757.
WEIGLE, J. & SAINI, H. (1936). *Helv. Phys. Acta,* **9**, 515.

X-ray Studies of the NaCl: SrCl2 System

BY E. LAREDO AND E. DARTYGE

*Sección Física, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas, Venezuela*

High-temperature diffraction experiments have been carried out on the NaCl: SrCl2 system, both in its poly- and monocrystalline form. These experiments have led us to the determination of the dilution enthalpy of the SrCl2 precipitates in the NaCl matrix ($h_D = 0.90 \pm 0.05$ eV). Brauer's method was used to calculate the distortion around one defect and Eshelby's model was used to evaluate the resulting change in the lattice parameter due to these perturbing centers. The concentrations of defects calculated from these models are in good agreement with those determined chemically. Small-angle X-ray scattering experiments were performed on the same crystals, with suitable thermal treatments, to follow the clustering of defects as a function of the annealing temperature. It is possible to maintain a large amount of nearly dispersed strontium in the lattice by quenching the crystals from high temperature. The point defects agglomerate by successive annealings from 100 to 300°C, forming clusters of increasing sizes. A discussion of the composition of those centers is included.

Introduction

The behavior of defects in doped alkali halides has been observed by numerous techniques: ionic conductivity (Dreyfus & Nowick, 1962; Brown & Hoodless, 1967); I.T.C. (Cappelletti & Benedetti, 1967); optical absorption (Cappelletti, 1968); thermal diffusion (Allnatt & Chadwick, 1967); dielectric losses (Cook & Dryden, 1962); e.p.r. (Bergé, Gago, Blanc, Benveniste & Dubois, 1966) and X-rays (Benveniste, Laredo, Bergé & Tournarie, 1965; Lilley & Newkirk, 1967). X-rays studies of defects have been used less frequently than the other techniques since they need a high concentration of defects ($\sim 1\%$ in molar concentration). We have been able to grow highly doped NaCl crystals with SrCl2 ($c < 3 \times 10^{-2}$) in which certain zones are single crystals. X-ray diffraction experiments and low-angle scattering experiments have been carried out on these crystals, complemented by ionic conductivity measurements on the same crystals (Laredo & Dartyge, 1970). At room temperature in very slowly cooled crystals, the Sr^{2+} ions exist in two states: as substitutional

ions in the lattice, and as cubic SrCl2 precipitates in the NaCl matrix. The precipitates have, as in the case of LiF: MgF2 (Lilley & Newkirk, 1967), an orientation relation with the matrix which in our case is

$$\{100\} \text{ NaCl } || \{100\} \text{ SrCl}_2$$
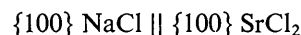
as determined by rotating-crystal photographs of these crystals.

At higher temperatures the precipitates re-dissolve, thus augmenting the number of Sr^{2+} ions in the lattice and the positive vacancies necessary to maintain the electrical neutrality of the crystal. These two types of defects, if they remain next to each other, form the dipole Sr^{2+} [Na$^+$]. At the temperatures used in our experiments, the ionic conductivity, which is sensitive to the number of free vacancies, shows that the degree of association Sr^{2+} [Na$^+$] is low. The defects that are present in the matrix give rise to a lattice distortion which can be followed by lattice-parameter measurements in the appropriate range of temperature. More-