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Energy Calculations for the Lattice Dynamics of NH_4IO_3

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The lattice dynamics of ammonium iodate have been studied experimentally and theoretically for centre-zone phonons. The frequencies of normal modes have been measured by Raman spectroscopy. The experimental results have been used to obtain the parameters of a simplified rigid-ion model. It is shown that the strongest bonds are the linear I–O and N–H covalent interactions, while the low-frequency external NH_4–IO_6 mode is mainly ionic in character. The effective ionic charge of the NH_4 group is −0·82 e.

1. Introduction

Ammonium iodate crystallizes with a perovskite-type structure. Of the many compounds with this structure, only a few possess cubic holohedral symmetry. The distortions of the structure may be caused (Cochran, 1960) by the competition of short-range and long-range interactions, leading in some cases to ferroelectric behaviour. In the sense of lattice dynamics, this fact must be attributed to the appearance of critical modes. Of these the simplest are the Slater and the Last modes, which have been found in tetragonal $BaTiO_3$. On the other hand, the iodates show the predominant influence of the short range (I–O) forces (Salje, 1973 *a,b*). Therefore the NH_4IO_3 structure can be understood as a distorted framework of linked octahedra, in which the 12-fold coordinated gaps have been filled. To allow comparison with other perovskite-like compounds such as $SrTiO_3$ (Cowley, 1964) Raman spectra of NH_4IO_3 were obtained and force-constant calculations carried out.

2. Experimental

Crystals up to 5 × 5 × 5 mm were grown by the convection method from aqueous solution at 35 °C. The dielectric constant of these crystals was measured by the zero-beat method to determine temperatures of phase transitions and is shown in Fig. 1. The increase of dielectric constant at lower temperatures and the presence of a singularity at −170 °C suggest the existence of a ferroelectric or antiferroelectric phase at low temperatures. A second phase transition at 82 °C can barely be seen in this diagram.

For the exact determination of this phase transition at 82 °C, piezoelectricity was measured at different temperatures (Salje, 1972). The temperature dependence of the piezoelectric coefficient d_{33} (Voigt notation) is shown in Fig. 2. It can be seen that NH_4IO_3 is acentric in both phases studied. The ratio $d_{33}/d_{11} \simeq d_{22} \leq 32$ indicates the presence of orthorhombic or tetragonal pseudosymmetry. The exact symmetry is probably lowered to *m*, 2, or 1.

Measurements of the lattice dynamics of NH_4IO_3 in the temperature range 20 to 150 °C were carried out by Raman spectroscopy with an apparatus described earlier. The low-frequency part of the spectrum is shown in Fig. 3. Additional spectral bands were found near 1422, 1670, 3050, and 3150 cm^{-1}, associated with internal NH_4 modes (Ananthakrishnan, 1937). In the first part of the spectrum 26 lines could be resolved. Hence the elementary cell must contain at least four formula units and a superstructure must be present. Moreover, the existence of a fourfold pseudoaxis means that the superstructure must be in the *ab* plane. The observation of six scattering signals with polarisation A_{zz} indicates a doubling of the *c* parameter. Thus NH_4IO_3 must have an eightfold unit cell.

The A_{zz} lines vanish in the high-temperature phase (Fig. 4). At temperatures above 120 °C additional Raman signals appear if crystals are exposed for a long time to a laser beam. The spectral distribution of these lines is similar to the spectrum of HIO_3 crystals and suggests that NH_4IO_3 decomposes above 120 °C.

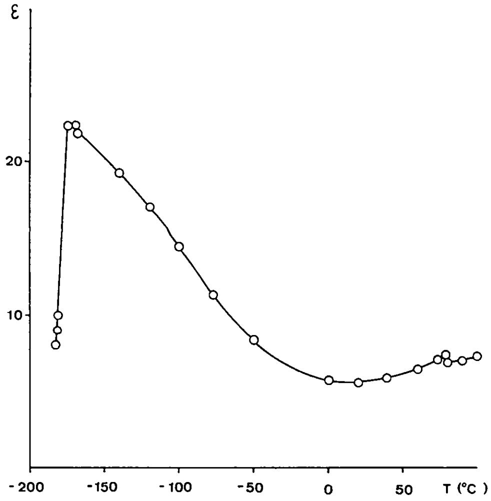


Fig. 1. Dielectric constant *versus* temperature. Phase transitions occur at −170 °C and 82·5 °C.

3. Energy interpretations of the Raman spectra

The rigid-ion model (Born & Huang, 1954; Woods, Brockhouse, Cowley & Cochran, 1963) was used for calculations in spite of the more satisfactory shell model (Cochran, 1960; Cowley, 1964), because:

(*a*) A calculation according to the shell model based on the observed unit cell requires 136 parameters. Even if we separate the internal interactions within the NH_4 groups, there are still 102 parameters to be considered.

(*b*) The neglect of polarization parameters connected with the shell of the cations introduces errors in the calculation of LO–TO splitting. However, because of the generalised LTS relation

$$\varepsilon_0 = n^2 \prod_i (\omega_i^2)_{\mathrm{LO}}/(\omega_i^2)_{\mathrm{TO}} \simeq 10 \qquad (1)$$

(Cochran, 1959) the LO–TO splitting is expected to be small.

We evaluated a dynamical tensor without consideration of shell parameters and fitted the coefficients to the experimental data. The secular equation is then:

$$m(K)\omega^2 = [R(KK') + Z(K)C(K'K)Z(K')] = D(KK'). \qquad (2)$$

In order to reduce the number of parameters, the separation of ionic modes, as suggested by Bhagavantam & Venkatarayudu (1969), was carried out. In the picture of the rigid-ion model this is equal to the assumption that the dynamical tensor can be obtained in the additive form:

$$D(KK') = D_{IO_6}(KK') + D_{IO_6-NH_4}(KK') + D_{NH_4}(KK'). \qquad (3)$$

The second term of this equation shows in the case of an *n*-fold unit cell only *n* non-vanishing eigenvalues.

To a first approximation these tensors have been constructed on the basis of group theory. A diagonal tensor of second degree with elements identical to the squares of the measured Raman frequencies was transformed by means of an inner automorphism. The transformation matrix T was chosen in such a way that the column vectors were the orthonormalized eigenvectors of the normal modes (Salje, 1973*a*,*b*). This approximation leads to:

$$D(KK') = T^{-1}(KK'')\omega(K''K''')T(K'''K). \qquad (4)$$

The dynamical tensor constructed in this way shows the same form as the matrix $R(KK')$, evaluated by Cowley for a zero wave vector. The splitting of LO–TO modes was taken into account in a second step with addition of the coulomb part of the interaction $Z(K')C(KK')Z(K)$. The values of the Coulomb coefficients $C(K'K)$, computed by means of the Ewald transformation, were taken from the work of Cowley (1962) for the undisturbed perovskite structure. The values of $Z(K)$ were fitted to the measured LO–TO splitting.

In the bigger unit cell, only short-range interactions of first order were taken into account and the dynamical tensor $D(KK')$ splits into 3×8 components along the major diagonal. The linear superposition (3) was assumed to hold in this case too.

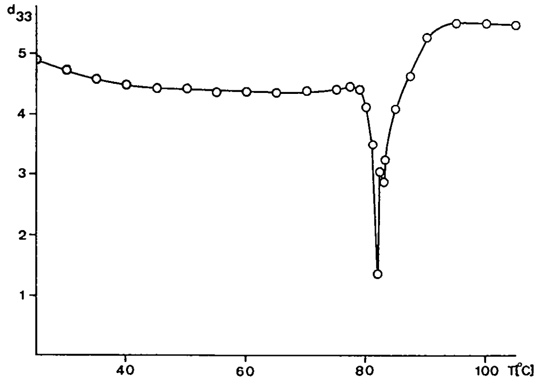


Fig. 2. Dependence of the piezoelectric coefficient d_{33} on temperature.

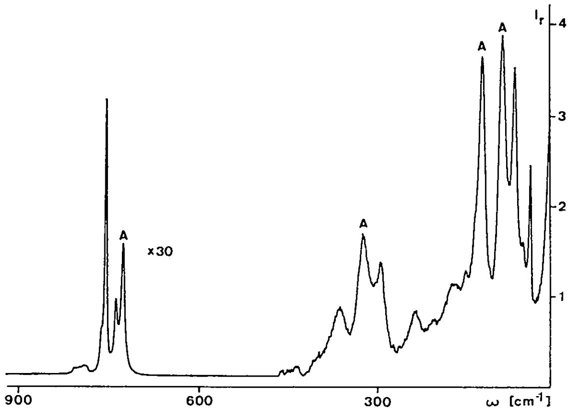


Fig. 3. Low-frequency part of the Raman spectrum of NH_4IO_3. The anti-Stokes lines mainly polarized in A_{zz} are indicated with A.

4. Calculation of valency constants with rigid NH_4 groups

The assumption of linear superposition of the dynamical tensors with respect to the separated interactions enables the calculation of a number of valency constants without consideration of internal NH_4 modes in the high-frequency part of the Raman spectrum.

In the low-energy part it was not possible to resolve all the lines because of the large unit cell. Hence only the lines given in Table 1, which have been unequivocally identified, were used for the calculations. From the polarization measurements lines belonging to three, spectrally well defined bands could be indexed as A_{zz}, B, and $A+B$ in accordance with the orthorhombic pseudosymmetry. Therefore the valency constants evaluated from these frequencies split into three groups which have to be correlated with irreducible representations B, A, $B+A$. A consideration of the additional phonon frequencies will not affect the calculated values of the valency constants, because the maximum shift in their wave numbers is only 4 cm^{-1}.

Table 1. *The wave numbers of $q \simeq 0$ optical modes in ammonium iodate from Raman spectroscopy*

ω	Polarization	$\omega[cm^{-1}]$	Polarization
53·3	–	300·0	B
80·2	B (TO)	326·7	A
103·4	A (TO)	370·3	$A+B$
133·0	$A+B$ (TO)	730·1	A
160·2	B (TO)	740·0	B
175	(LO)	760·2	$A+B$
240	(LO)		

For comparison with literature data the valency parameters have been normalized in terms of Cowley's parameters:

$$\left(\frac{\partial^2\varphi}{\partial r^2}\right)^i_{\parallel} = \frac{e^2 A_i}{2V} \; ; \quad \left(\frac{\partial^2\varphi}{\partial r^2}\right)^i_{\perp} = \frac{e^2 B_i}{2V} \qquad (5)$$

where $i=1$ for the ionic part, $i=2$ for iodine–oxygen interaction, and $i=3$ for pure-oxygen force constants. The calculated values are listed in Table 2.

Table 2. *The parameters of the simplified rigid-ion model*
The unit of the short range forces is $\frac{1}{2}e^2$ V^{-1}.

Interaction	Valency	A	B	$B+A$
NH_4–IO_6	A_1+B_1	4·4	3·7	7·8
I–O	A_2	279	288	300
O–O	A_3+B_3	60	60	60
I–O	B_2	−17	−24	−5

$Z_{NH_4} = 0{\cdot}75$–$0{\cdot}9$ e.

The values of the effective ionic charges have been evaluated from the TO–LO splitting of the ionic modes. A splitting of the other spectral bands due to Coloumb forces could not be detected. For this reason, the iodine–oxygen interaction was assumed to be of short-range character. The effective charge of the NH_4 group is then computed to be $-0{\cdot}82$ e. The contribution of ionic forces to the valency is then, in the approximation of a 'diagonal cubic' crystal, 8·4 e^2 V^{-1}. Hence it is stronger than the short range part $A_1+B_1 \simeq$ 5·3 e^2 V^{-1}. Thus the character of the NH_4–IO_6 bond will be approximately 60% ionic, whereas the I–O bond can be considered purely covalent.

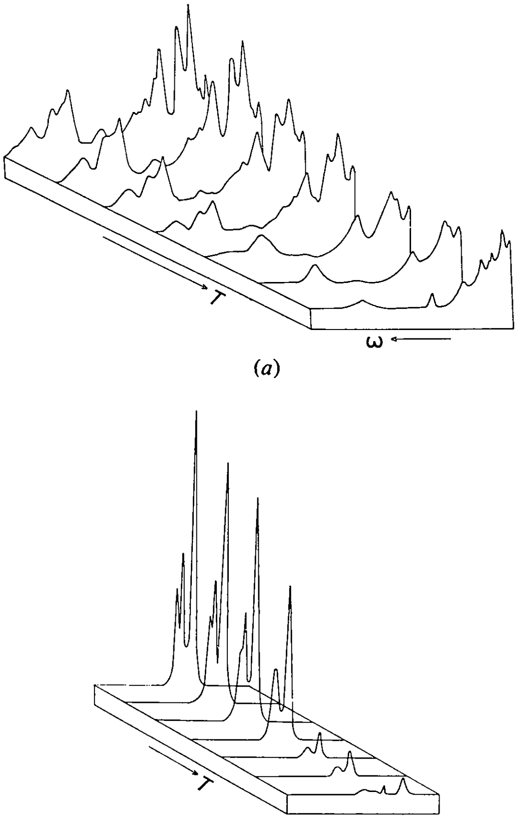
The dominant part of the valency must be attributed to the A_2 value, just as in the case of $SrTiO_3$. This value is nearly five times as big as all other constants (Table 2). Thus oxygen is strongly bonded to iodine. The negative value of $B_2 \simeq -15$ e^2 V^{-1} shows that torsional distorsions of the octahedral complexes are favoured leading to deviations from ideal cubic symmetry. In contrast to the ferroelectric phase of $BaTiO_3$, where there is a considerable displacement of the central atom due to the critical behaviour of the Slater mode, NH_4IO_3 appears to possess mainly tilted octahedra, similar to KIO_3 (Hamid, 1973; Salje, 1973*a*,*b*).

It can be assumed that these energy relations are true in principle for all thermodynamic phases of NH_4IO_3. According to the theory of soft-mode behaviour the only possible critical mode for the transition to the ferroelectric low-temperature phase is the well-known ionic Last mode.

The splitting of the valency constants in various directions (Table 2) must be attributed to the real structure of NH_4IO_3. An exact analysis is possible only if the structure is known.

5. Character of NH_4 tetrahedral bonds

The possible eigenvibrations of a tetrahedral group in an isotropic crystal field can be derived from the molecular symmetry T_d with the irreducible representations A_1+E+2T_2. The corresponding normal coordinates are to be evaluated for the isolated complex in terms of internal coordinates. They could be taken from the work of Di Bartholo (1968). In the special case of



(*a*)

(*b*)

Fig. 4. Raman spectra at various temperatures (*a*): 30 cm^{-1} to 400 cm^{-1}; (*b*): 630 cm^{-1} to 900 cm^{-1}. The spectra were measured at 20, 50, 75, 80, 100, 125, and 150°C.

NH_4IO_3 the number of irreducible representations is eightfold because of the chosen unit cell. The higher-symmetry representations split according to the local symmetry into lower-dimensional representations. Among the possible point groups, D_{2d}, D_2, C_{2v}, and C_s have been selected as representatives for further consideration. The splitting in these groups is shown schematically in Table 3. The total number of expected Raman lines follows from the consideration that the sum of all irreducible representations with respect to their dimension must be equal to the dimension of Γ. The number of Raman lines for the point groups have been computed and are listed in Table 4.

Table 3. *Correlation scheme for the irreducible representations of a tetrahedral complex*

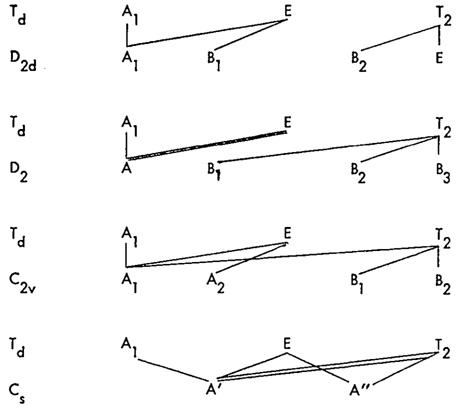


Table 4. *Number of Raman lines for internal* NH_4 *modes*

T_d	D_{2d}	D_2	C_{2v}	C_s	obs	ω[cm^{-1}]
8	8	8	8	8	3	3050
8	8+8	16	8+8	8+8	6	1670
8	8+8	8+8+8	8+8+8	16+8	7	3130
8	8+8	8+8+8	8+8+8	16+8	6	1422

In agreement with these calculations four spectral bands are found experimentally. The multiplicity of lines was 3, 6, 7, and 6. Some of these lines are found to be strongly dependent on polarization. Therefore the NH_4 groups are not rotationally free in the room-temperature phase. The symmetry must be determined by the point groups listed in Table 4.

The valency constants of normal modes were calculated by analogy with the octahedral complex. Only internal coordinates were used because of the small influence of the anisotropic crystal field. With the notation

$$\frac{\partial V}{\partial r} = K\frac{e^2}{V}\,;\quad \frac{\partial V}{\partial \varphi} = \Delta\frac{e^2}{V} \tag{6}$$

the well-known relationship for the eigenfrequencies is:

$$K = m_H\omega_1^2\,;\quad \Delta = \tfrac{1}{3}m_H\omega_2^2\,. \tag{7}$$

The characteristic volume is in this case the volume of the cube enclosing the tetrahedral complex. Both the valency constants determine all four phonon frequencies. To test the validity of this theory the equation

$$\frac{\omega_3\,.\,\omega_4}{\omega_1\,.\,\omega_2} = \sqrt{\frac{2}{3}\left(1+\frac{4m_H}{m_N}\right)} \tag{8}$$

was used. The agreement between the calculated values [right-hand side of (8)] and those of the observed centres of the peaks [left-hand side (8)] is better than 0·2%. Hence, the three most accurately determined values of the valency constants are

$K = 133$ 143 146 $e^2\,V^{-1}$

$\Delta = 13{\cdot}8$ 14·3 14·5 $e^2\,V^{-1}$.

These values are comparable with those of the A_2–B_2 constants of the octahedral complex. Like the latter, they show, in effect, two different valency constants. The reasons for this can be discussed only when the exact structure is known.

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