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Thermal Contraction in NH$_4$IO$_3$ and its Significance with Respect to the Phase Transition

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NH$_4$IO$_3$ shows an abrupt contraction in the direction of spontaneous polarization at 82°C. This anomaly is accompanied by changes in the optical properties and phonon spectra, which were also studied at different pressures. On the basis of the lattice parameters and Raman spectra a probable mechanism is suggested for the phase transition.

Introduction

Iodates with large ions such as K, Rb and Cs, possess perovskite-like structures with distorted octahedral coordination for I. Those with smaller ions like H, Li and Na show other structures, in which the typical octahedral framework of the perovskite is lacking. The latter are characterized by pyramidal IO$_3^-$ ions. The structure of NH$_4$IO$_3$ (Keve, Abrahams & Bernstein, 1971) is noteworthy because it shows the characteristics of both types, namely pyramidal IO$_3^-$ ions occur in a distorted perovskite-like structure, thereby giving rise to interesting physical properties. Some of these were studied by Crane, Bergman & Glass (1969) and Salje (1974b) who observed a phase transition at 85°C. The aim of this study is to understand the nature of the transformation and to test if NH$_4$IO$_3$ is really ferroelastic as suggested by Keve *et al.* (1971).

Experimental

The phase transformation of NH$_4$IO$_3$ was studied by X-ray, optical and Raman spectroscopic methods at different temperatures and pressures. The variation of the lattice constants with temperature was studied with a focusing Guinier-type camera. The orientation relations between the different lattices were studied with a precession camera by heating single crystals on an iron–constantan thermoelement to about 100°C.

The refractive index n_β was measured at room temperature by the immersion method and the birefringence with a Zeiss compensator. The optical orientation and the optic axial angle were determined with an universal stage which could be heated to about 120°C. The transition temperature could be determined accurately by measuring the changes in the birefringence with a laser beam as source of light in a conoscopic arrangement and a photomultiplier to measure the changes in the intensity of the transmitted light.

The dependence of the phonon spectra on hydrostatic and uniaxial pressure and temperature was determined in a Raman experiment described earlier (Salje, 1974a). Hydrostatic pressures up to 1·5 kbar were produced in a heatable steel vessel with corundum windows and with argon as the pressure medium. Higher pressures up to 20 kbar were applied in a piston cylinder apparatus with windows made of corundum, mounted in a small furnace. Uniaxial pressures were obtained by keeping the crystal in a heatable forceps. The pressure was varied by tightening a screw.

Results

NH$_4$IO$_3$ shows two phase transitions, one at 82°C and the other at about 115°C. At room temperature the following optical parameters have been observed:

$$n_\alpha = 1·777; \quad n_\beta = 1·785; \quad n_\gamma = 1·826; \quad 2V = 48·2°.$$

The orientation of the indicatrix is: n_α, n_β and n_γ parallel to [100], [010], and [001] respectively. The optic character is positive. The optic axial angle $2V$ increased gradually on heating to a value 60·2° just

below the transition temperature. At the transition point, these axes disappeared and spontaneously new axes emerged giving a value of 84·5° for $2V$ of the high-temperature modification. The symmetrical displacement of the optic axes with temperature indicate an orthorhombic symmetry for the phases of NH_4IO_3, both above and below the transition temperature. The temperature of transformation determined while the probe was heated varied between 87 and 95°C for different crystals. However, all the probes showed the same temperature (82°C ± 2) on cooling. The transition temperature (82°C) was determined accurately by measurement of the change in birefringence with temperature.

The lattice parameters also vary with temperature. The lattice constants (Table 1) of the room-temperature modification agree well with those of Keve *et al.* **c** increases distinctly with temperature, **a** remains almost constant, and **b** shows a slight decrease. Thus **a** and **c** tend to become equal near the transition point. Above 82°C, there is a marked contraction in **b**.

Table 1. *Lattice constants of* NH_4IO_3 *(orthorhombic)*

Temperature (°C)	a (Å)	b (Å)	c (Å)	Volume Å³
20	6·403 (2)	9·168 (4)	6·337 (2)	374·6 (4)
80	6·413	9·156	6·411	376·5
83	6·426	9·104	6·466	378·3
120	9·113	9·113	9·113	756·8

The powder pattern changes at the transition point. The d spacings of the planes (020), (101) and ($\bar{1}01$) become equal. As their normals correspond to the edges of the strongly diffracting cubic subcell ($a \simeq 4·56$ Å), this would give the impression that the pattern can be indexed on the basis of a trigonal or rhombohedral
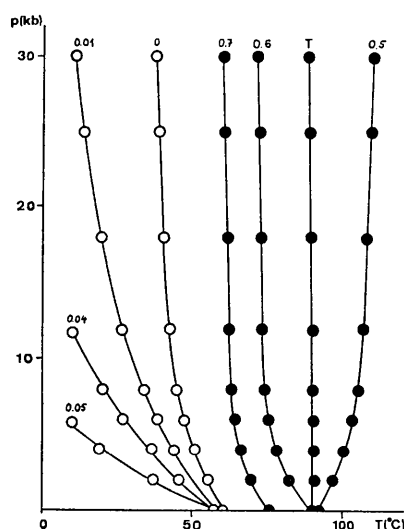

Fig. 1. Relationship of Raman scattering cross sections with temperature and pressure. The curves connect points with the same intensity ratios (open circles represent I_A/I_B; filled circles represent I_B/I_{A+B}, $T=$ transition point).

lattice. However, a subsequent examination of single crystals with a precession camera revealed that the superstructure reflexions indicating the doubling of **b** do not disappear and that the symmetry remains orthorhombic. This is in accordance with the optical behaviour.

At about 115°C, many reflexions of the pseudo-trigonal lattice of the high-temperature form spontaneously coincide, so that the pattern can be indexed on the basis of a cubic lattice with $a=4·56$ Å, except for the presence of two very weak reflexions. This transformation could not be observed so distinctly by other methods.

The transition temperature and the nature of transition were also studied by Raman spectroscopy. According to Salje (1974b) the most important lines which are affected by the transition and those with frequencies 730·1 (A); 740·0 (B), 300·0 (A), 326·7 (B), 760·2 ($A+B$), and 370·3 cm^{-1} ($A+B$). They have been divided into three groups A, B, and $A+B$ on the basis of their polarization behaviour. With increasing temperature the scattering intensity of the A peaks decreases. At temperatures above 62°C they could not be detected. The intensities of all the other lines remain nearly unaffected. The frequencies of all detectable phonons remain constant up to the transition point at 82°C. The B peaks disappear here abruptly and two new lines appeared with frequencies 313 cm^{-1} and 735 cm^{-1}. They agree well with the mean values of A and B modes.

If a pressure (about 50 bar) was applied in the direction of the spontaneous polarization [010], the transition temperature was lowered to about 70°C for a few crystals. But a similar application of pressure even up to 100 bars parallel to [100] and [001] did not produce any change. A direct observation of ferro-elastic behaviour could not be made at the pressures applied. At higher pressure the crystals were destroyed. An examination of the ferroelectric behaviour at different pressures showed no hysteresis loop up to fields of 8 kV cm^{-1}.

The crystals subjected to a pressure of 20 kbar showed an interesting P–T relationship (Fig. 1). It can be seen that the relative intensities of the individual phonon signals show a remarkable dependence on pressure; with increasing pressure they indicate that the polarizability of I changes as the transition point is approached. However, the transition temperature is practically independent of pressure. Moreover, no pressure-induced transformation could be found.

The fact that high hydrostatic pressures had only a small effect on the phonon frequencies up to about 75°C means that the Grüneisen parameter

$$\gamma = \frac{3\alpha V}{C_v K} \sim \frac{d \ln \omega}{d \ln V}$$

must have very low values. α is the linear coefficient of thermal expansion, C_v is the specific heat, V the volume, and K the compressibility. These parameters

have been separately determined and the results are illustrated in Figs. 2 and 3. C_v being 26 cal deg^{-1}, the Grüneisen constant is found to vary between 0·3 and 0·7. It must be noted that the smaller values are given by lower pressures. They are found to be at least five times smaller than those of the alkali halides. They were checked with the formula of Slater using compressibilities alone,

$$\gamma = -V/2(\partial^2 p/\partial V^2)/(\partial p/\partial V) - \tfrac{2}{3} \simeq 0·6.$$

The two values of γ agree well, which means that the bond energies in NH₄IO₃ are practically unaltered during compression.

Discussion

The structure of NH₄IO₃ is a highly distorted perovskite-like structure. The IO₆ octahedra are deformed such that three O atoms are much closer together than the others. The structure is characterized by torsions of the octahedra, causing an antiparallel orientation of the smaller faces of the octahedra. This torsion gives rise to the symmetry operation 2_1. The I atoms are displaced from the centre of the deformed octahedra nearly parallel to the body diagonal of the cubic subcell producing pyramidal IO₃ ions instead of IO₆ complexes.

The phonon spectra of NH₄IO₃ can be interpreted on the basis of the pyramidal IO₃ ions. The three different groups of lines (Salje, 1974b), correlated to three different valency parameters, are indexed by a splitting of a trigonal E mode into the phonon branches A and B. The second trigonal A mode causes the peak $A + B$. The small splitting of the E mode in the Raman spectrum of the room-temperature phase results from the deviation of the symmetry of the IO₃ ions from trigonal. This splitting vanishes at the transition point. Therefore it is assumed that the local symmetry of the IO₃ pyramid is now trigonal. This assumption is also compatible with the relationship that must exist between the measured frequencies (Herzberg, 1945).

A consideration of I–O lengths of the room-temperature phase suggests how the trigonal symmetry of the IO₃ ion can be achieved. They are 1·806, 1·836, and 1·765 Å respectively and are approximately proportional to the lengths of the corresponding a (4·53), b (4·58), and c (4·51 Å) axes of the cubic subcell. This proportionality can be expected because of the direct linking of the O octahedra. It can be seen from Fig. 4 that c_s increases comparatively rapidly with temperature and becomes almost equal to a_s below the transition point. At the transition temperature b_s also contracts, the lattice becoming pseudotrigonal. A similar behaviour of the corresponding I–O length will give the local trigonal symmetry to the pyramidal IO₃ ions.

A true trigonal symmetry is, however, impossible for the entire structure because of the existence of the 2_1 axis, even at higher temperatures, as indicated by the superstructure reflexions. Hence the I–O distances of
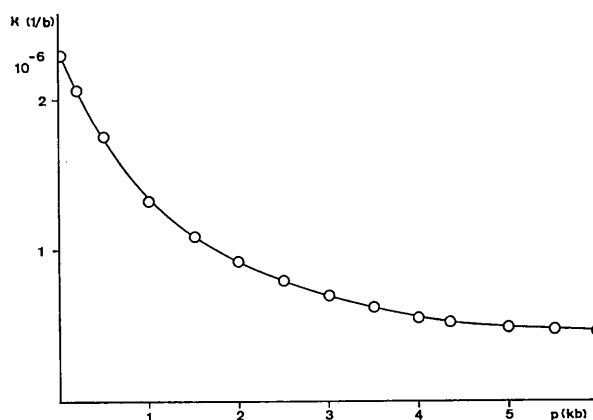

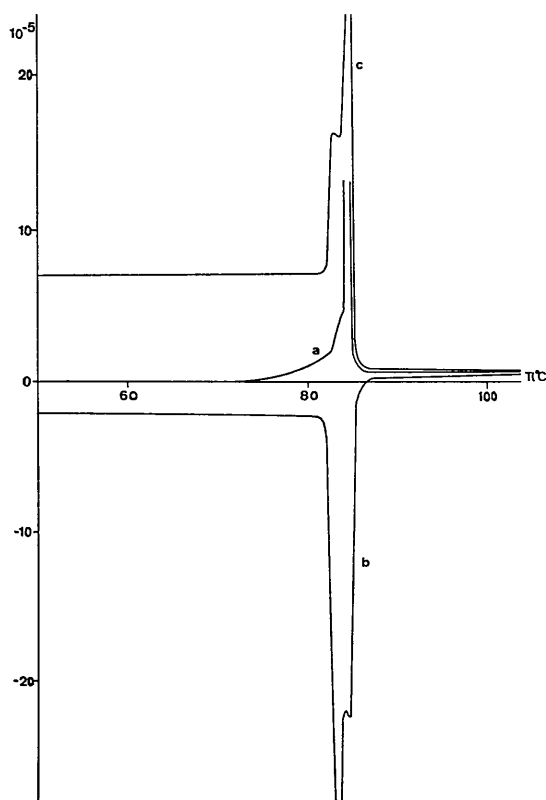Fig. 2. Compressibility of NH₄IO₃ *versus* pressure.

Fig. 3. Variation of the thermal expansion coefficient with temperature.
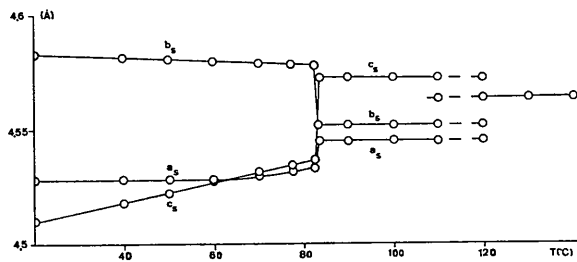

Fig. 4. Variation of the hypothetical lattice parameters of the cubic subcell, $a_s = a_{or}/\sqrt{2}$, $b_s = b_{or}/2$, $c_s = c_{or}/\sqrt{2}$.
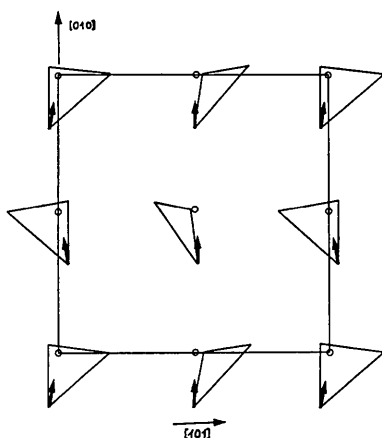
Fig. 5. A graphical illustration of the transformation mechanism. The arrows represent the transformation vectors. Only one layer of the IO_3 pyramids is shown.

the proposed structure for the high temperature form will be about 1·78 Å for the shorter and 2·83 Å for the longer bond. The important transformation vectors can be seen in Fig. 5. This mechanism will lead to smaller and more regular IO_3 pyramids compared to the room-temperature form. As the contracting I–O bond is nearly parallel to **b**, it must cause a small shrinkage parallel to **b**.

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The Application of Direct Methods to Centrosymmetric Structures containing Heavy Atoms. II

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Direct methods are applied to the difference structure factors for a structure containing one or more heavy atoms in known positions. For those reflexions whose sign is determined by the heavy atoms, the known heavy-atom contribution is subtracted from the observed structure factor to obtain the magnitude and the sign of the light-atom contribution. The signs of the reflexions that do not have an appreciable heavy-atom contribution are found using the Σ_2 sign relationship. For reflexions with an intermediate heavy-atom contribution the sign and magnitude ambiguity is also solved by the Σ_2 formula. Thus it is possible to maximize the number of correct signs, and correct some of the amplitudes, before a difference Fourier map is calculated.

Introduction

In paper I (Beurskens & Noodik, 1971) direct methods were used to solve the phase problem for those special cases where the heavy atoms are on special positions, such that the heavy atoms do not contribute to several reflexion parity groups. In those cases the crystal structure is not determined by the positions of the heavy atoms only: one or two phases have to be chosen in order to specify the origin fully.†

The present paper deals with the general case: the positions of the heavy atoms completely determine the

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† A Fortran program for the execution of this procedure, *DIRDIF.A*, is now available on request.

structure; the phase problem is solved in principle: the positions of the remaining 'light' atoms can be found by standard Patterson and Fourier techniques. The time and effort necessary for finding the light-atom structure is reduced by the present procedure, especially when the heavy atoms are marginally sufficient to solve the phase problem.

Define:

$|F_{obs}|$ is the observed structure factor.

F_H is the calculated contribution of the known part of the structure ('heavy' atoms).

F_L is the contribution of the remaining part of the structure ('light' atoms).

$S(F)$ is the sign of F.