Raman spectroscopy studies on the orthorhombic-to-rhombohedral transition in thallous nitrate

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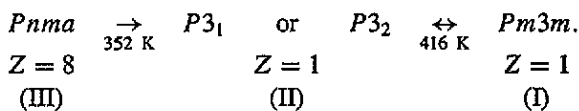† High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay 400085, India
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Abstract. The external modes of thallous nitrate have been studied as a function of temperature for oriented single crystals. Since the orthorhombic→rhombohedral transition ($T_{tr} = 352$ K) is irreversible, the spectra of both phases could be recorded at low temperatures for the same crystal. Two distinct nitrate librational bands are identifiable in the orthorhombic phase corresponding to the two sets of nitrate ions. These are observed to be centred at 120 and 145 cm^{-1} at 100 K. Across the transition temperature, while the former remains unshifted, the band at 145 cm^{-1} is observed to soften abruptly and in the rhombohedral phase it is also found to occur at 119 cm^{-1}. Structurally, this would therefore imply reorientation of one of the two sets of nitrate molecules. The enumeration of external modes in the rhombohedral phase rules out the possibility of a unit cell with one formula unit per unit cell, as it has been assumed in the literature so far.

1. Introduction

Thallous nitrate belongs to the class of heavy ion alkali nitrates such as $CsNO_3$ and $RbNO_3$. Interest in this class of nitrates has centred around the proposed martensitic nature of the rhombohedral→cubic transition (Kennedy and Patterson 1965, Kennedy and Kriven 1981). There has been a considerable amount of ambiguity regarding the structure of the rhombohedral phase of $TlNO_3$ although it is assumed to be isostructural to the rhombohedral forms of the other two nitrates (Stromme 1971, Fraser *et al* 1975). The transition sequence in $TlNO_3$ accepted to date has been

$$Pnma \quad \xrightarrow{352\ K} \quad P3_1 \quad \text{or} \quad P3_2 \quad \xleftrightarrow{416\ K} \quad Pm3m.$$
$$Z = 8 \qquad\qquad\qquad Z = 1 \qquad\qquad\qquad Z = 1$$
$$\text{(III)} \qquad\qquad\qquad \text{(II)} \qquad\qquad\qquad \text{(I)}$$

Consequently, the latent heat of transformation at 352 K is attributed to the large volume change ($\Delta V \simeq 10\%$) across the transition (Kennedy and Patterson 1965, Bury and McLaren 1969). Kennedy and Patterson (1965) show that the orthorhombic (III)-to-rhombohedral (II) transition is kinetics dominated and, under suitable conditions of heating, the transition proceeds by the formation of a habit plane perpendicular to the orthorhombic b axis. The trigonal threefold axis is expected to be contained in the $(110)_0$ plane. They called this mechanism the 'coherent' mechanism of transformation. As will be discussed later, this gives rise to an important question regarding the orientation of the nitrate groups in the rhombohedral phase. Since the nitrates in the cubic phase are expected to be dynamically

disordered and, further, since the rhombohedral unit cell was expected to be derived from the cubic unit cell by a very small distortion along the cubic [111] axis, nitrate disorder in the rhombohedral phase also seemed plausible.

The room-temperature structure of thallous nitrate has been fairly well established from single-crystal x-ray diffraction studies (Fraser *et al* 1975). The important aspect of their elucidation of the structure has been the fact that the nitrates are distributed into two sets of four ions each. The planes are these two sets of nitrates are either parallel or perpendicular to the σ_h mirror of the orthorhombic unit cell. This has been further substantiated by the vibrational spectra analysis from infrared and Raman measurements on single crystals (Pogarev and Shultin 1973). Figure 1 shows the disposition of the two sets of nitrates when viewed along the orthorhombic a, b and c axes.
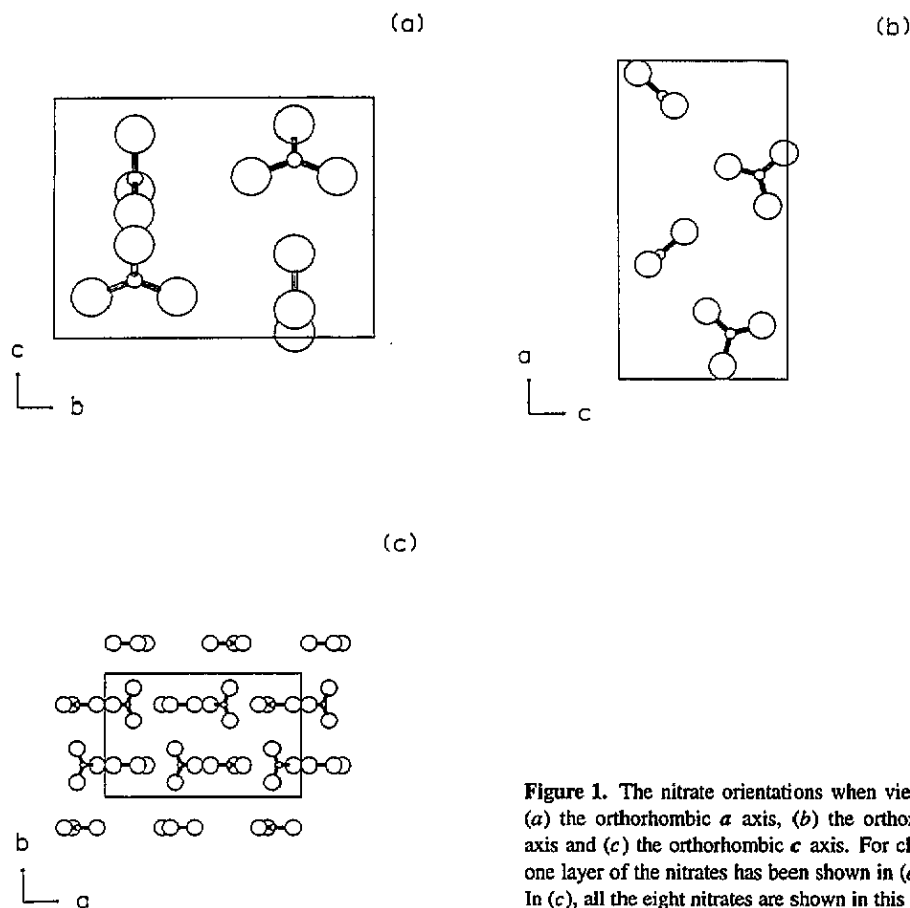

Figure 1. The nitrate orientations when viewed along (*a*) the orthorhombic *a* axis, (*b*) the orthorhombic *b* axis and (*c*) the orthorhombic *c* axis. For clarity, only one layer of the nitrates has been shown in (*a*) and (*b*). In (*c*), all the eight nitrates are shown in this projection.

Most of the Raman studies done on the transitions in $TlNO_3$ so far have been restricted to powder samples (Brooker and Irish 1970, Brooker 1971, James and Devlin 1971) and have not addressed the structural mechanisms of the phase transitions explicitly. This work is therefore the first attempt at obtaining Raman spectra as a function of temperature on oriented single crystals. Since the nitrates are expected to be disordered in the cubic phase and therefore the librational modes are expected to be heavily damped, no meaningful

conclusions can be derived from the study of Raman spectra in this phase. The work has therefore been restricted to the study of the orthorhombic-to-rhombohedral transition.

2. Experimental details

Single crystals of $TlNO_3$ were grown by the slow cooling of a solution of $TlNO_3$ in water, from high temperatures, with urea as the growth modifier. Details of the growth and characterization have been reported elsewhere (Somayazulu *et al* 1988). After identifying the required crystallographic directions on an x-ray precession camera, the appropriate faces were cut and polished. Both right-angled geometry and back-scattering geometry were used to obtain spectra for various polarizations of the incident and the scattered radiation.

Raman spectra were recorded using the 5145 Å line ($P \simeq 100$ mW) from an indigenously built flow-type Ar^+ ion laser using a double-grating spectrograph in the photon-counting mode (Roy and Bansal 1988). Temperature variation was effected through a glass-walled high-temperature cell. The spectra at 100 K were recorded using a double-walled glass cryostat. The temperature was controlled using a PID controller to a precision of ± 1 K. The sample temperature was measured using a standard chromel–alumel thermocouple. Figure 2 shows the Raman spectra at different temperatures in the $X(ZZ)\bar{X}$ geometry. The optical quality of the crystal is known to deteriorate on transforming to the rhombohedral phase, if heated rapidly. After repeated trials, we have found that a heating rate of 0.5 K min^{-1} is slow enough to preserve the optical quality of the transformed crystals. The spectra recorded in the $X(YZ)\bar{X}$ geometry, for the same temperatures is shown in figure 3. For the low-temperature studies, the spectra of the orthorhombic phase (phase III) at 100 K were first recorded for different polarizations. After completion of transformation at 352 K the same crystal was mounted on the cryostat and cooled to record the spectra of the rhombohedral phase (phase II) at 100 K. This was possible since the III→II transition is irreversible in nature. Pairs of the low-temperature spectra are shown in figures 4 and 5 for (ZZ) and (YY) polarizations. The polarization directions X, Y and Z are taken to be coincident with the orthorhombic unit cell axes a, b and c, respectively.

3. Discussion of results

Group-theoretical analysis of the normal modes in phase III (*Pnma*; 8 formula units/cell) yields the following result for the external modes:

$$9(A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u}).$$

The Raman-active external modes can be classified as follows:

$$\text{librations} : 2A_g(xx, yy, zz) + 4B_{1g}(xy) + 2B_{2g}(zx) + 4B_{3g}(yz)$$

$$\text{translations} : 7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g}.$$

Therefore, according to the selection rules, Raman-active libration modes occur in all the polarizations. They are indeed seen in the spectra (zz, yy and yz) presented. Further, since both sets of nitrate ions have the site symmetry m in the crystal, the libration modes also belong to identical irreducible representations. Thus, from symmetry considerations alone, it is not possible to distinguish between the two sets of nitrate ions. In order to obtain detailed
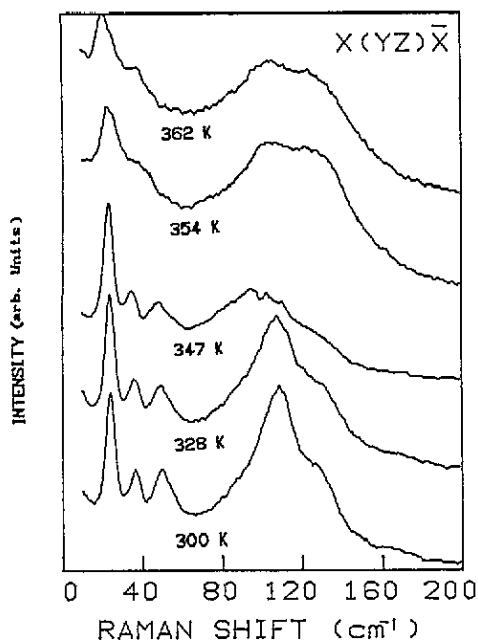
Figure 2. Raman spectra in the $X(ZZ)\bar{X}$ geometry as a function of temperature, and across the transition at 352 K. The polarization directions here and elsewhere are with reference to the orthorhombic unit-cell axes.
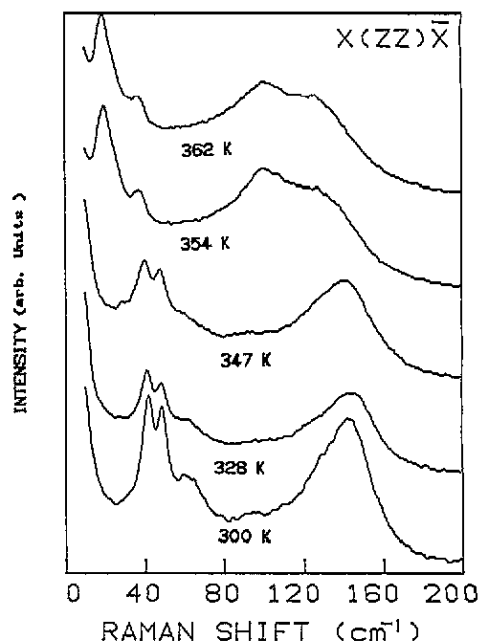
Figure 3. Raman spectra in the $X(YZ)\bar{X}$ geometry as a function of temperature and across the transition at 352 K.

information about the eigenvectors, lattice-dynamical calculations have been performed for the orthorhombic phase of $TlNO_3$ within the framework of the rigid-ion model by employing the computer code DISPR (Chaplot and Rao 1980). Using the results of these calculations, the two prominent bands at 120 and 145 cm^{-1} (cf figures 4 and 5) are identified as nitrate librational bands. Although the two nitrate groups in $TlNO_3$ are not symmetry related, the calculations indicate that their motion is not mutually exclusive. In other words, one may not be able to attribute unambiguously the librational bands at 120 and 145 cm^{-1} to one or the other nitrate groups. However, on the basis of the calculated amplitudes of displacement of the molecules, it can be argued that the relative contribution of the nitrates perpendicular to the σ_h mirror to the band at 145 cm^{-1} is dominant. As is evident from figure 2, this band is observed to soften abruptly across the transition whereas the other librational band (120 cm^{-1}) remains virtually unshifted (cf figure 3). We see from figures 4 and 5 that the librational band frequencies are better defined at low temperatures. From these spectra, frequencies corresponding to the main librational bands are estimated as 120 cm^{-1} (FWHM, 12 cm^{-1}) and 145 cm^{-1} (FWHM, 10 cm^{-1}) in phase III and 119 cm^{-1} (FWHM, 14 cm^{-1}) in phase II. In figure 5, we have shown the Raman spectra of both the phases at 100 K in the $X(YY)Z$ polarization. As can be seen, the two spectra are virtually indistinguishable. Further, only the 120 cm^{-1} librational band is observed to be active in this polarization, in both the phases. Although the data for other polarizations have not been presented, we have collected the spectra as a function of temperature in $Z(XY)\bar{Z}$, $Z(XX)Y$ and $Z(XZ)Y$ polarizations also. It has been confirmed in all the scattering geometries that the nitrate librational band in the rhombohedral phase always occurs at 119 cm^{-1}. Further, the spectra in the rhombohedral phase clearly show that the cell multiplicity is greater than unity. As
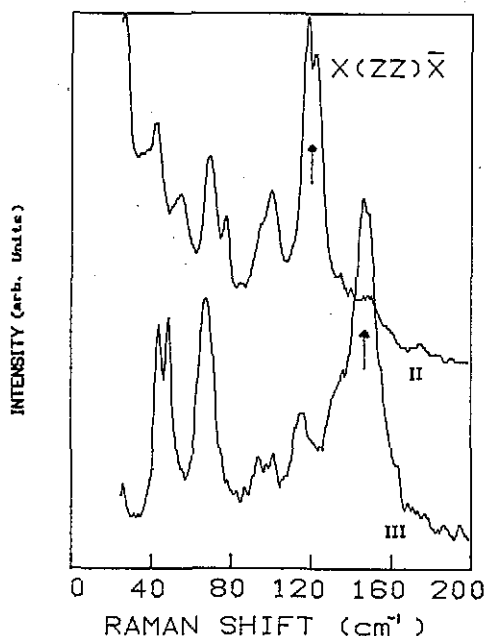
Figure 4. Raman spectra recorded at 100 K in the $X(ZZ)Y$ geometry of both phase III and phase II. The mean positions of the nitrate librational bands in the two phases are indicated by the arrows.
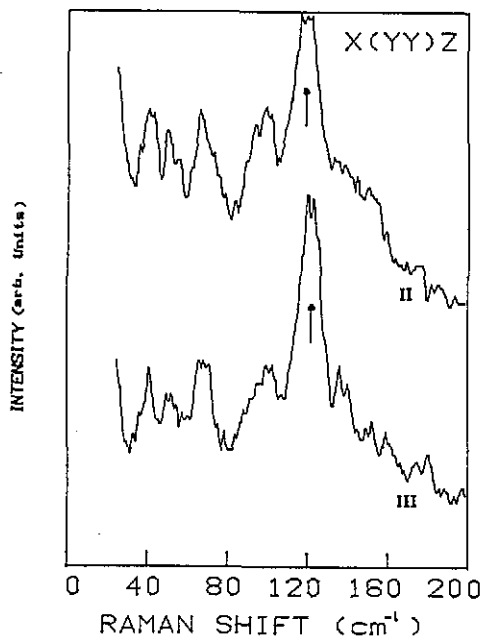
Figure 5. Raman spectra recorded at 100 K in the $X(YY)Z$ geometry of both phase III and phase II. The mean positions of the nitrate librational bands in the two phases are indicated by the arrows.

can be seen from figures 2 and 3, librational bands show significant broadening in the vicinity of the transition and in phase II. This implies that the nitrates undergo disordering around the transition point and in phase II. However, as is seen in figures 4 and 5, the librational bands in both the phases have similar half-widths at low temperatures, indicating that the disordering is induced at high temperatures and is arrested at low temperatures.

From the reports in the literature (Brown and McLaren 1969) that the powder x-ray diffraction pattern of phase II can be indexed in terms of a hexagonal cell with $Z = 9$ (or equivalently by a $Z = 3$ rhombohedral cell), we propose the following construction for the rhombohedral cell:

$$a_r = \tfrac{1}{2}(a_0 + b_0) \tag{1.1}$$

$$b_r = -\tfrac{1}{4}a_0 + \tfrac{1}{2}b_0 + \tfrac{1}{2}c_0 \tag{1.2}$$

$$c_r = -\tfrac{1}{4}a_0 + \tfrac{1}{2}b_0 - \tfrac{1}{2}c_0. \tag{1.3}$$

In this, the rhombohedral [111] axis is assumed to be coincident with the orthorhombic b axis. Accepting the above construction of the rhombohedral cell, it is now found to be crystallographically impossible to continue having two distinct nitrate groups, since all the nitrate threefold axes are expected to lie parallel to the rhombohedral threefold axis. Structurally this would therefore imply that the nitrates lying perpendicular to the σ_h mirror in phase III must reorient such that they lie on a plane perpendicular to the trigonal axis in phase II across the transition. The experimental observation that only one of the nitrate

librational bands undergoes an abrupt jump across the transition fits well with such a model of selective reorientation of nitrates. That is, only one set of nitrates reorients across the transition, while the other set remains undisturbed, resulting in all nitrates having an identical orientation in phase II. Consequently, in the rhombohedral phase, only a single nitrate librational band is expected since all the nitrates are now symmetry related. This is well corroborated by our experimental observations that the nitrate librational band in phase II occurs only at 119 cm^{-1}. It may be noted here that our model for the $\text{III} \rightarrow \text{II}$ transition in TlNO_3 may give the impression that the change in structure is solely due to changes in the rotational degrees of freedom of one set of nitrates. However, we have observed the appearance of a new lattice mode at 16 cm^{-1} in phase II. This mode is likely to be due to Tl^+ translational motion, which implies that the $\text{III} \rightarrow \text{II}$ transition in TlNO_3 involves displacements of the Tl^+ ions from their orthorhombic positions. One may therefore expect rotational–translational couplings to play some part in the transition mechanism.

Acknowledgment

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