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TEMPERATURE DEPENDENCE OF IR ANALYSIS OF $Sr(NO_3)_2$

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ABSTRACT

The infrared spectra of $Sr(NO_3)_2$ have been thoroughly investigated under normal pressures and at different temperatures during its phase transition II → I at ~ 320 °C. The study includes measurements and interpretations of the IR spectral band shape, intensities and frequencies of the internal modes as functions of temperature. Special attention is paid to the bending mode ν_2, the asymmetric stretching mode ν_3, the first overtones ($2\nu_1$, $2\nu_3$) and the combination mode ($\nu_1 + \nu_4$). The results reveal that the transformation from the ordered state (phase II) to the disordered state (phase I) of $Sr(NO_3)_2$ can be monitored by clear variations in the spectral parameters for ν_2, ($2\nu_1$, $2\nu_3$), ν_3 and ($\nu_1 + \nu_4$) modes. According to the IR analysis reported here, the energy barrier of the reorientation of the NO_3^- ions is found to be 0.29 eV in the ordered phase II and 0.28 eV in the disordered phase I.

INTRODUCTION

The crystal structures of $Sr(NO_3)_2$ have been fairly widely studied both in the high temperature and low temperature regions [1]. These crystals were found to be isostructural with the cubic space group *Pa*3, with four structural units in the unit cell, the eight NO_3^- ions occupying sites with point symmetry C_3. In the absence of external forces, the nitrate ion forms a planar equilateral triangle [2,3]. In its centre is the nitrogen atom, while the oxygen atoms are at the vertices.

According to Hubert [4] the arrangement of metal ions in the crystal structure of $Sr(NO_3)_2$ corresponds to a cubic face-centred Bravais lattice. They are connected by nitrate groups with the N atoms on the three-fold axes and are twelve-coordinated by O atoms. The coordination polyhedron around M^{2+} can be visualized as a considerably distorted cuboctahedron with broken square faces.

The nature of the temperature dependence of thermal activity of the NO_3^- group is of great interest as its role is fundamental in explaining many of the physical properties of this complex compound. The possibility of reorientational motion of the NO_3^- group has been investigated by neutron diffraction methods [5,6], but no free rotation of the NO_3^- ions about their

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three-fold axes was detected. The temperature dependence of the d.c resistivity and dielectric constant of polycrystalline samples of $Sr(NO_3)_2$ was found to show anomalies in the high temperature region [7]. In addition, sharp peaks were obtained in both differential thermal analysis (DTA) and thermomechanical analysis (TMA) curves. The TMA curve for $Sr(NO_3)_2$ showed a pronounced peak at 325 ° C. This peak was related to a sudden increase in the expansion coefficient associated with the rotation of the NO_3^- group leading to a solid state phase transformation.

Brooker and Irish [8] studied the infrared and Raman spectra in a room temperature phase powder sample of $Sr(NO_3)_2$. The vibration observed can be interpreted conveniently in terms of a factor group analysis and considerable band structure is reported for the first time. Correlation field splittings are of the order of 50 cm^{-1} in the antisymmetric stretching region, whereas in the region of the symmetric stretch, antisymmetric bend and out-of-plane deformation correlation field splittings are of the order of 2 cm^{-1}. The magnitude of these splittings is essentially that of those observed for univalent metal nitrates [9,10].

We consider that infrared spectroscopy might be used to confirm the observed phase changes, and we report here an investigation of IR analysis of the phase transition in $Sr(NO_3)_2$ samples.

EXPERIMENTAL

IR spectra were recorded using a Beckman GR 7224 spectrometer and the experimental techniques employed have been reported [11]. The material used was ultra-pure $Sr(NO_3)_2$ (BDH, England). Samples used were in the form of discs, prepared by mixing 2.5 mg of $Sr(NO_3)_2$ with 1 mg of KBr in a cylindrical die of 10 mm diameter. The die was then evacuated to ensure dryness and the sample was pressed. The spectra were recorded in the region 4000–400 cm^{-1} on graphical paper with a scanning time of 30 min.

RESULTS

IR spectra of $Sr(NO_3)_2$ were obtained in the range 30–400 ° C. Herzberg's notation [12] was used for the internal fundamental normal modes of vibrations of NO_3^-. Thus ν_1 denotes the totally symmetric stretching mode, ν_2 the out of phase deformation, ν_3 the doubly degenerate asymmetric stretch, and ν_4 the doubly degenerate in-plane deformation of the NO_3^- ion. The IR spectrum observed at room temperature showed no band which could be attributed to any model other than those due to ionic fundamentals of the NO_3^- group. The accuracy of frequency measurements is estimated to be ± 1 cm^{-1} for sharp peaks and about ± 10 cm^{-1} for very broad bands.

TABLE 1

Infrared spectra of $Sr(NO_3)_2$ in the ordered and disordered phases

Frequency assignment (cm^{-1})	Ordered phase II (°C)						Disordered phase I (°C)		
	30	200	250	300	310	320	330	350	400
ν_4	738	735 s	735 s	735 s	735 s	732 s	730 s	730 s	730 s
ν_2	830 s	815 s	815 s	812 s	815 s	812 s	810 s	810 s	810 s
ν_1	1055 w	1060 w	1055 w	1055 w	1055 vw	1050 vw	1050 vw	1050 vw	1050 vw
	1090 w	1100 sh	1100 sh	1090 sh	1100 sh	1090 sh	1090 sh	1095 sh	1095 sh
ν_3	1375 b	1365 b	1380 b	1360 b	1365 b	1375 b	1375 b	1375 b	1375 b
$2\nu_4$	1470 sh	–	–	–	–	–	–	–	–
$2\nu_2$	1635 b	1650 sh	1635 b	1635 b	1650 sh	1650 sh	1650 sh	1650 sh	1650 sh
$(\nu_1+\nu_4)$	1790 s	1790 s	1795 s	1790 s	1790 s	1795 s	1795 s	1795 s	1795 s
$2\nu_1$	2080 b	2080 b	2140 b	2140 b	2140 b	2130 b	2130 b	2120 b	2120 b
$(\nu_1+\nu_3)$	2450 w	2450 b	2460 b	2460 b	2460 b	2440 b	2450 b	2450 b	2450 b
$2\nu_3$	2810 b	2830 b	2820 b	2820 b	2820 b	2810 b	2810 b	2800 b	2800 b

s = Sharp; b = broad; sh = shoulder; w = weak; vw = very weak.

IR spectra were obtained here at 30 (room temperature RT), 200, 250, 300, and 320 °C for the ordered phase II and at 330, 350, and 400 °C for the disordered phase I. The frequencies of each band of the NO_3^- ion and their assignments are collected in Table 1.

The IR spectrum of the ordered phase II and disordered phase I is shown in Fig. 1. Figure 2 shows the doubly degenerate symmetric stretch ν_3 in $Sr(NO_3)_2$, appearing as a broad band centered at ~ 1380 cm^{-1} in the

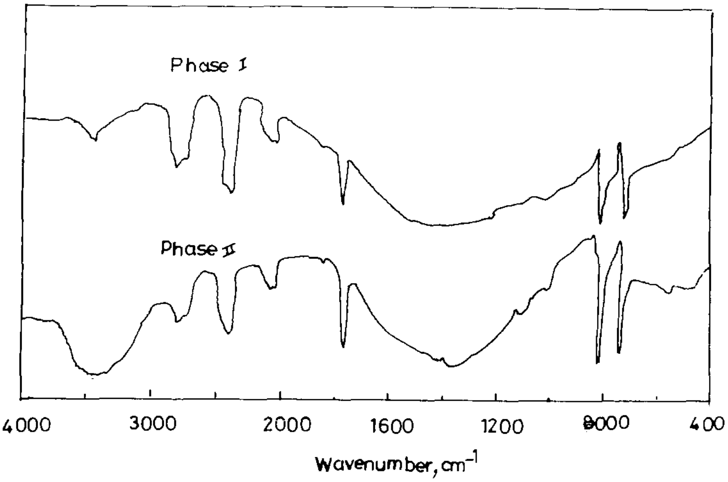

Fig. 1. IR bands of NO_3^- group of $SR(NO_3)_2$ in phases I and II.

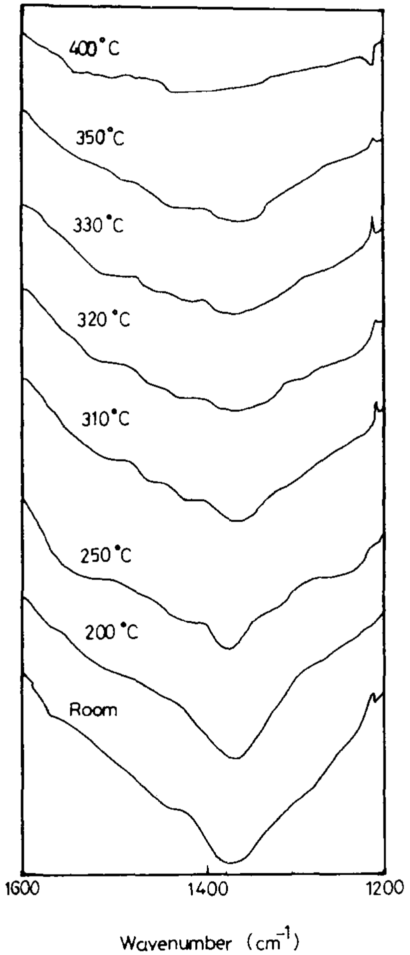

Fig. 2. Temperature dependence of the ν_3 band of the NO_3^- group of $Sr(NO_3)_2$.

ordered phase while in the disordered phase the mode ν_3 increases in the broadening shape and is centered at ~ 1375 cm^{-1} as the temperature is increased.

The combination mode ($\nu_1 + \nu_4$) appearing at ~ 1790 cm^{-1} was found to be sensitive for both ordered and disordered states (Fig. 3).

At room temperature the peak height showed its maximum value; at 200 °C and above, the variation in the peak height is small (slight increase). However, at 320 °C maximum peak height was recorded again. This maximum value of the peak height intensity of the IR mode ($\nu_1 + \nu_4$) is considered to be an indication for the transformation of the sample to the disordered state. Further heating does not greatly affect the peak height. Also, the combination mode ($\nu_1 + \nu_3$) (Fig. 4) appeared at ~ 2450 cm^{-1}, showed a reduction in the integrated intensity up to ~ 320 °C (ordered

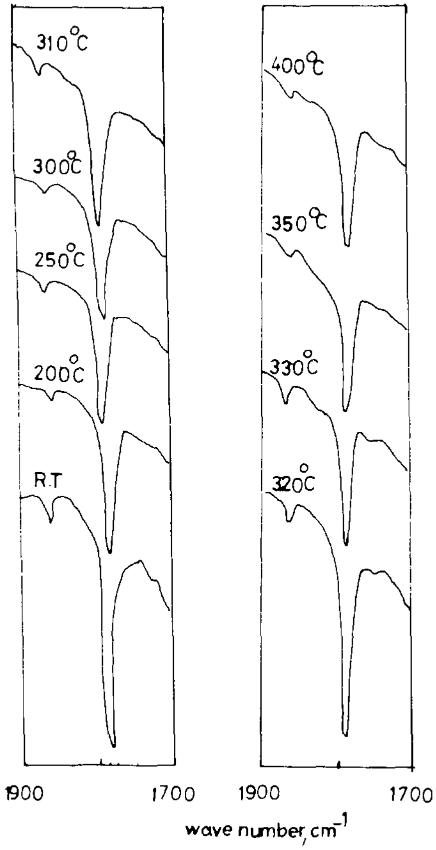

Fig. 3. Temperature dependence of the combination mode ($\nu_1+\nu_4$) of the nitrate ion of $Sr(NO_3)_2$.

phase II), and then increased in the disordered phase I as the temperature increased.

The first overtones ($2\nu_4$) of mode ν_4 appeared at room temperature only, and disappeared completely above room temperature. The overtone $2\nu_2$ (1635 cm^{-1}) showed some shift in the disordered phase I (~ 15 cm^{-1}). Also, the overtone $2\nu_1$ appeared here at 2080 cm^{-1} and shifted to ~ 2130 cm^{-1} with rising temperature. The overtone $2\nu_3$ appeared here as a broad band of non-symmetric shape at ~ 2820 cm^{-1} and as the temperature increased a downward wave number shift occurred such that this overtone appeared at 2800 cm^{-1} at 350 °C, as shown in Fig. 5(a, b).

In the region 900–700 cm^{-1} in the IR spectra of $Sr(NO_3)_2$ two bands were observed (ν_4 ~ 738 and ν_2 ~ 830 cm^{-1}) in the ordered phase II. Both ν_4 and ν_2 are less sensitive both for ordered and disordered states.

The peak intensities of these two bands decreased with rising temperature up to 310 °C; at 320 °C the peak height of the two bands increased with increasing temperature as shown in Fig. 6(a, b).

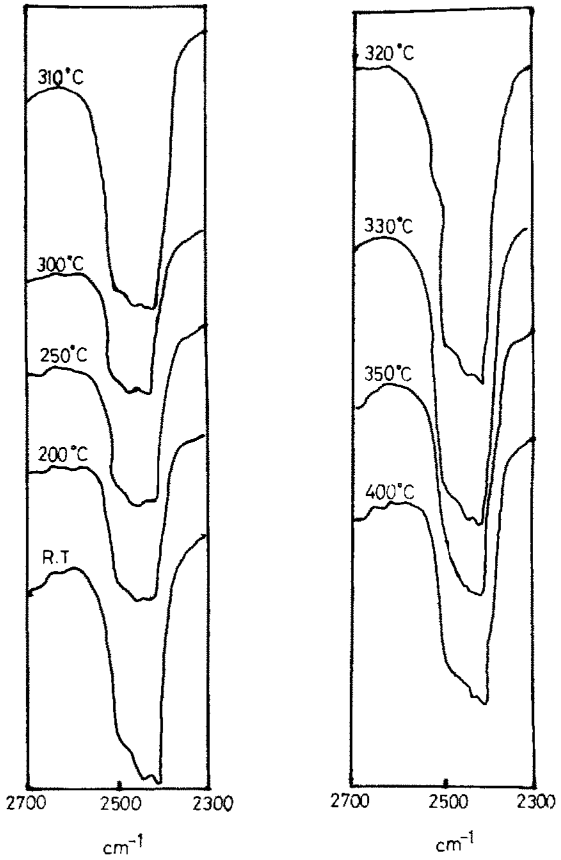

Fig. 4. Temperature dependence of the combination mode ($\nu_1 + \nu_3$) of the nitrate group of $Sr(NO_3)_2$.

It may be seen from our results shown in Figs. 2–6 that the transformation from the ordered state in $Sr(NO_3)_2$ to the disordered state was shown by clear variations in the characteristics of the vibrational modes ν_3, ($\nu_1 + \nu_4$), ($\nu_1 + \nu_3$), $2\nu_1$, $2\nu_3$ and ν_2 as the phase transformation temperature (~ 320 °C) is achieved. As a confirmation, the change in the relative integrative intensities of these modes with temperature has been studied and the results are shown in Fig. 7.

Maximum integrated intensity could be observed at the phase transition point. Thus one can discern that it is possible to confirm the existence of a phase transition by studying the temperature dependence of the IR bands. The change in band contours of the IR spectrum in the well established ν_3, ($\nu_1 + \nu_4$) bands and the overtones bands $2\nu_1$ and $2\nu_3$ of the NO_3^- ion shown in Figs. 1–4 strongly support this important result. Thus one can consider that a major change in model characteristics of the IR bands takes place near the phase transition point (~ 320 °C) of $Sr(NO_3)_2$ which could be

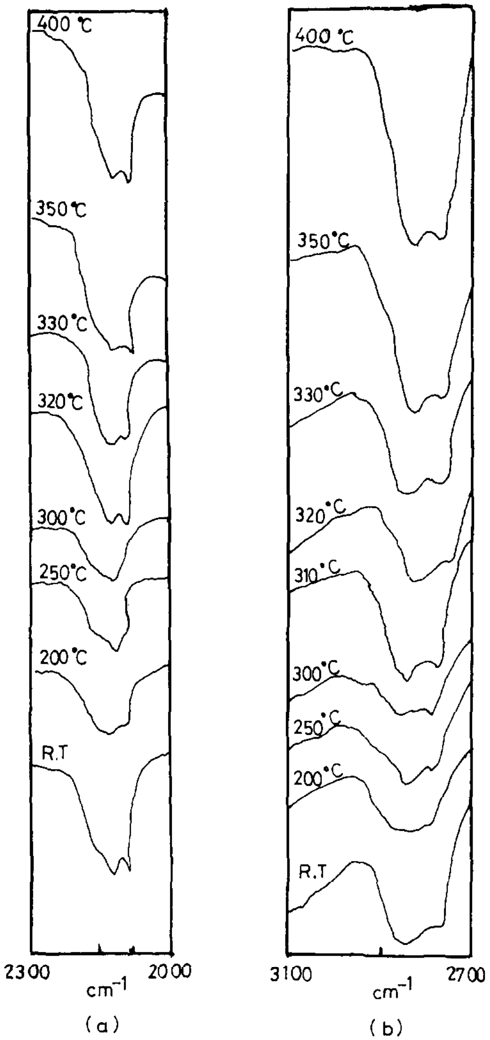

Fig. 5. (a) Temperature dependence of the first overtone $2\nu_1$ of the nitrate group of $Sr(NO_3)_2$. (b) Temperature dependence of the first overtone $2\nu_3$ of the nitrate group of $Sr(NO_3)_2$.

taken as an indication of the beginning of the orientational motion of the nitrate group in the lattice studied by IR analysis. Consequently this could be considered as a simple indication of the beginning of the disordered state in the system.

The energy barrier separating two different orientations of the NO_3^- group in the two phases II and I can be determined by using the relaxation time equation given by [13] $\tau = \tau_0 \exp(U/KT)$, where U is the rotational barrier energy, K the Boltzmann's constant and T is the absolute temperature in the region of ν_2.

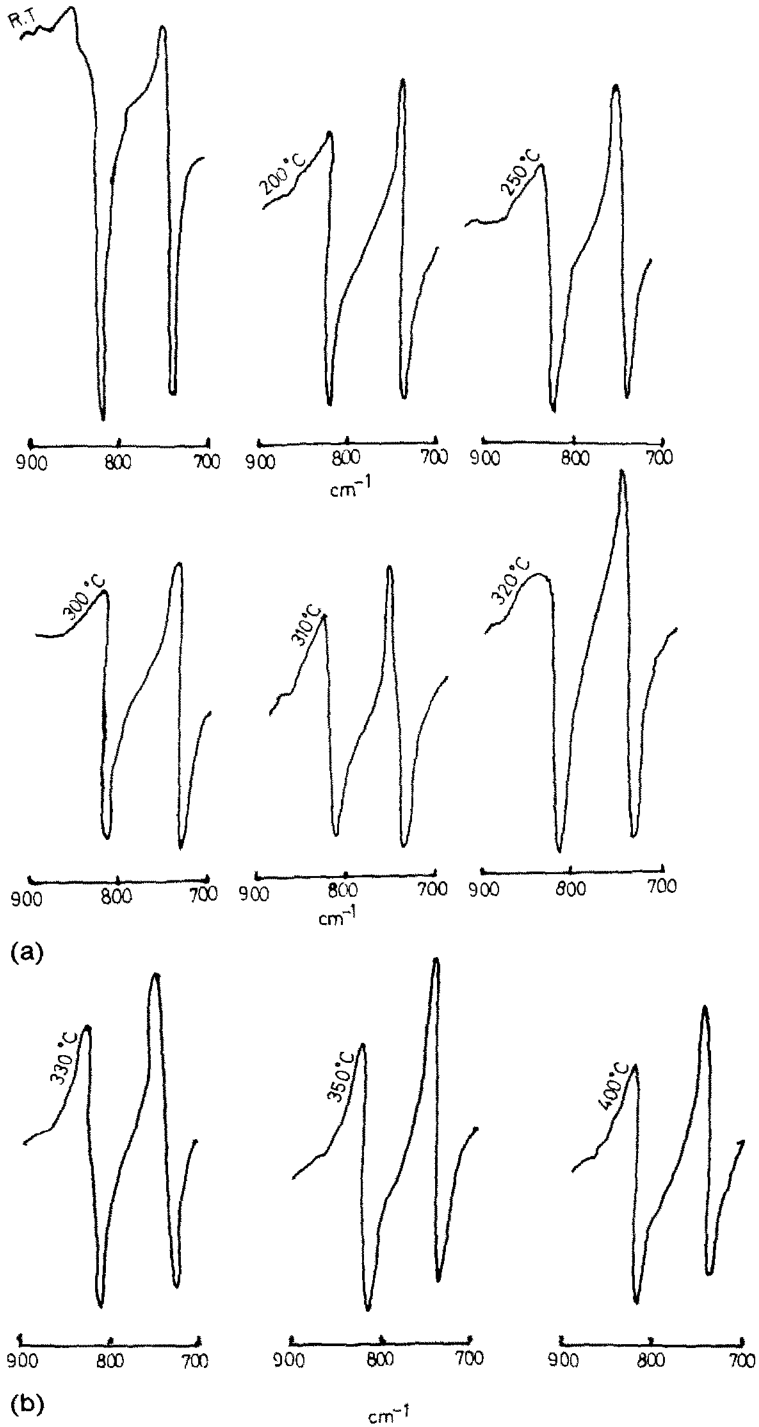

Fig. 6. (a) The variation of the IR spectra for the internal bending mode ν_2 with temperature in the ordered phase II. (b) The variation of the IR spectra for the internal bending mode ν_2 with temperature in the disordered phase I.

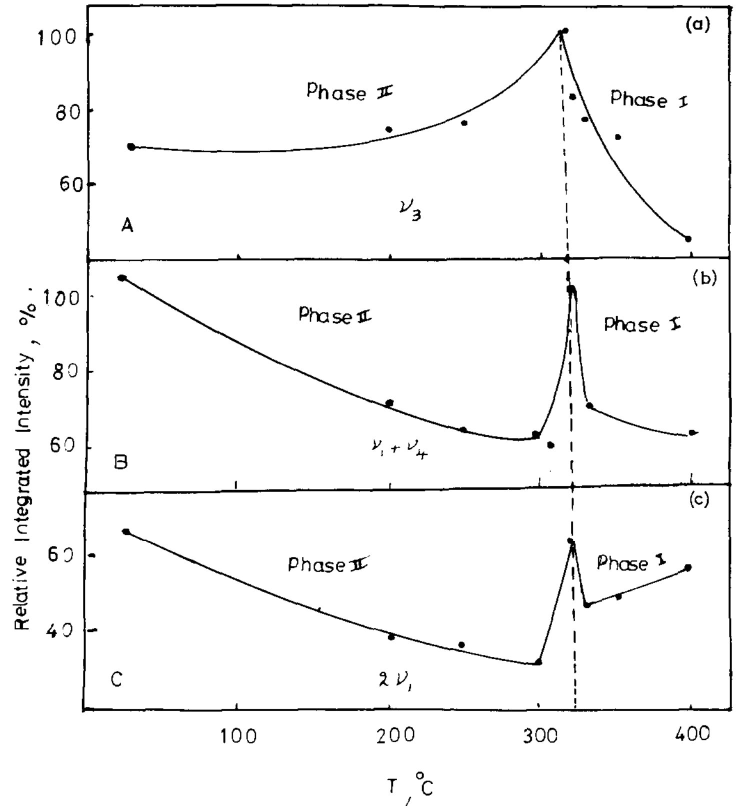

Fig. 7. Temperature dependence of the relative intensity for: (a): ν_3 mode, (b): combination mode ($\nu_1 + \nu_4$), (c): overtone $2\nu_1$ mode.

Figure 8 shows the variation of the rotational energy barrier with temperature. The relaxation time can be determined here by [14] $\tau = 1/\pi\ \Delta\nu C$, where $\Delta\nu$ is the half band width of the IR absorption band and C the velocity of light. The results of these calculations indicated that phase I was associated with an energy barrier 0.28 eV, while phase II was associated with an energy barrier of 0.29 eV.

DISCUSSION

A phase transition is considered as an interruption of the regularity of the thermodynamic functions characterizing the state of a substance at a special point called the phase transition point [15]. As soon as such a point is reached the initial phase can no longer exist and changes to a new phase. Near this critical point a substance acquires unusual properties. The phenomenon of disordering of molecules in crystal may be experimentally observed by studying the temperature dependence of the vibrational spectra in the region of internal vibrations of the molecules as well as in the region of external lattice vibrations. The probability of reorientation of the mole-

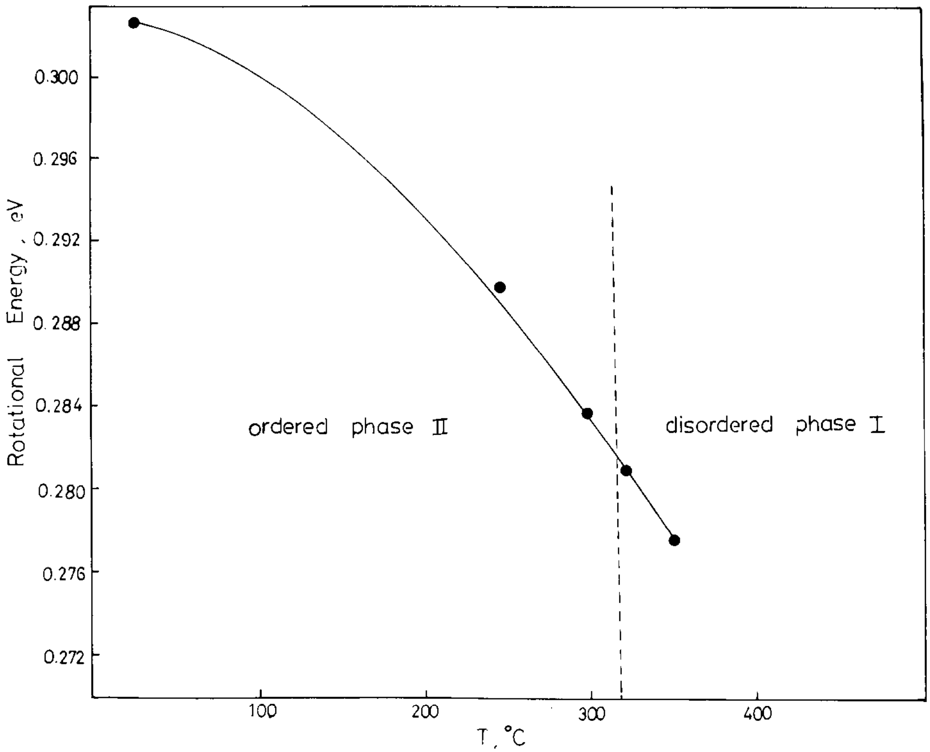

Fig. 8. Temperature dependence of the rotational energy barrier in the region of ν_2.

cules considerably increases with increasing temperature, especially near the transition point. At the phase transition, the character of the reorientation changes qualitatively, and this should lead to a change of the characteristics of the vibrational spectrum of the crystal.

From the above considerations, it was thought reasonable to study the spectroscopic effects related to the process of disordering principally by studying the IR absorption spectrum characteristics of the nitrate group. Also, the study of the effect of the temperature on the IR absorption spectra allows important information about the dynamics of the processes of disordering to be obtained which is important in understanding the nature of the order–disorder phase transition in both monovalent and divalent metallic nitrates.

At room temperature $Sr(NO_3)_2$ has a space group T_h^6–$Pa3$ with four formula units per unit cell [16]. The nitrate ion is on a C_3 site while the cations are on S_6 sites. With increasing temperature thermally-activated reorientational processes are accompanied by lessening or weakening of the ionic bonds which may promote the formation of dipoles whose partial rotation is permissible and is associated with further expansion of the lattice. This effect increases with temperature, and the expansion reaches its maximum value at about 325 °C [7].

The unperturbed nitrate ion (D_{3h} symmetry) would generate the following spectrum; $\nu_1(A_1')$ Raman active around 1050 cm^{-1}, $\nu_2(A'')$ infrared active around 825 cm^{-1}, $\nu_3(E')$ and $\nu_4(E')$ both Raman and infrared active around 1380 cm^{-1} and 720 cm^{-1}, respectively. From the factor group analysis above, it can be seen that for cubic nitrate crystals: (a) ν_1 should split into two Raman active modes and a non-coincident infrared band; (b) ν_2 should have a single infrared band and two non-coincident Raman modes; (c) both ν_3 and ν_4 should split into three Raman active and two noncoincident infrared bands [17].

A feature which is common to all of the infrared spectra recorded at various temperatures (in both ordered and disordered phases) is the sharpness of the out-plane bending vibration $\nu_2(A_2'')$ and also the broadening of the asymmetric stretching mode $\nu_3(E')$, whatever the temperature. However, it is well known that the distinct shape of an absorption band for a particular molecule is related to the number of ions that undergo the various energy transitions. Thus, the most intense line is that which represents the largest number of ions undergoing a particular transition. Figure 7(a, b and c) shows the variation of the intensity of the ν_3, $(\nu_1 + \nu_4)$ and $2\nu_1$ modes with temperature. Since the intensity of each band depends on the number of ions undergoing a certain energy transition, the band envelope as a whole is representational of the total number of ions involved [18]. As the temperature of the ions increased, the contour of the absorption band will change and the area under the envelope changes provided that the increase in temperature changes the number of NO_3^- ions initially in the vibrational level $\nu = 0$.

One of the combinations of the NO_3^- ion bands observed in the region 2500–1700 cm^{-1} is the $(\nu_1 + \nu_4)$ mode. In spite of the fact that the asymmetric in-plane bending mode ν_4 could not be individually detected, its combination with ν_1 was readily observed in both the ordered phase at ~ 1790 cm^{-1} and disordered phase at ~ 1795 cm^{-1}. To explain the anomalous behaviour of the $(\nu_1 + \nu_4)$ band (Fig. 7(b)), it is proposed that the NO_3^- ions are oriented in a disordered fashion and the rate of orientation increases with temperature due to thermal agitation. The increase in the rate of reorientation of NO_3^- is reflected as a decrease in the band intensities of the combination mode $(\nu_1 + \nu_4)$. The ratio of the intensities of these bands in two phases could be used to judge the degree of disorder of anions in the region of the phase transition II → I. At high temperature the asymmetry in the shape of the combination mode $(\nu_1 + \nu_4)$ (apparent on the high frequency side) is improved (Fig. 3). The asymmetry in the IR band shape could arise from the combination with the lattice mode [9] or from the coupling of the vibrational modes of NO_3^- groups or due to isotopically different forms of the NO_3^- ion [20].

All infrared spectra of $Sr(NO_3)_2$ obtained showed the presence of the important broad band ν_3. Schroeder et al. [21] have resolved this band for some nitrates at low temperatures and have assigned it as combination bands of the internal modes and an unspecified librational band. However, the observed strong inhomogeneous broadening of the ν_3 band is due to the difference between orientations of the individual NO_3^- ions. The phase transition II → I caused a gradual increasing in the broadening of the ν_3 band as the temperature increased, especially in the disordered phase (Fig. 2).

The height of the potential barrier U of the ordered phase II was found to be 0.29 eV, whereas that of the disordered phase I was found to be 0.28 eV. In fact both U and U' represent the potential barrier which must be crossed during the reorientation process. Also, $\Delta U = U - U'$ represents the activation energy of the ordered–disordered phase transition process and was found to be 0.01 eV. Thus besides the order position of the NO_3^- ions in the lattice existing at temperature below ~ 320 °C, these orientations are separated by a potential barrier of about 0.29 eV in the ordered state and 0.28 eV in the disordered state.

Increasing the temperature of $Sr(NO_3)_2$ crystals not only leads to a thermal population of the alternative orientations but also decreases the depth of the potential well.

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