Pramāṇa, Vol. 21, No. 1, July 1983, pp. 41–50. © Printed in India.

Laser Raman spectra of mixed crystals of $[(NH_4)_{1-x}K_x]_2SO_4$

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MS received 7 August 1982; revised 25 March 1983

Abstract. The Raman spectra of mixed crystals of $[(NH_4)_{1-x}K_x]_2SO_4$ in the region 50-3400 cm^{-1} at 293 K and below 223 K have been reported. At room temperature 293 K, as the concentration of K^+ ion increases in the crystal up to 50%, the frequencies of the totally symmetric vibrations of SO_4^{2-} and NH_4^+ ions increase and thereafter the frequency of SO_4^{2-} vibration decreases and attains the value in K_2SO_4. This change in frequency up to 50% of potassium concentration is due to the breaking of hydrogen bonds of the type N-H...O. The behaviour of Raman intensities of A_g (ν_1) mode of SO_4^{2-} for various concentrations ($x = 0, 0{\cdot}03, 0{\cdot}11, 0{\cdot}5, 0{\cdot}85$) suggest that the phase transition changes from first order type to one of second order. The phase transition in mixed crystals of $[(NH_4)_{1-x}K_x]_2SO_4$ can be a cooperative phenomenon arising from a coupling between $(NH_4)^+$ ions through hydrogen bonds with the distorted SO_4^{2-} ions in the low temperature phase.

Keywords. Laser Raman spectra; mixed crystals; hydrogen bond; infrared spectra; order-disorder.

1. Introduction

Ammonium sulphate undergoes a first-order ferroelectric phase transition at $T_c = 223$ K (Matthias and Remeika 1956; Hoshino *et al* 1958). The heat of transition and the change in entropy are $Q = 0{\cdot}93$ kcal/mole, $S = 4{\cdot}2$ cal/mole/deg (Hoshino *et al* 1958). The crystal exhibits an anomalous change in polarization; a very low value of Curie-Weiss constant (~ 15 K) (Unruh 1970) and a large spontaneous strain (Aniskatov and Martinov 1970).

Neutron diffraction, ESR, infrared (Jain *et al* 1973), NMR, Raman spectroscopy and dielectric methods have been applied to study the phase transition in ammonium sulphate. Based on the type of experimental technique used and the results obtained an order-disorder model (O'Reilly and Tsang 1967), an improper ferroelectric model (Ikeda *et al* 1973), a coupled oscillator model (Sawada *et al* 1973), a coupled-oscillator relaxator model (Petzelt *et al* 1974), a ferroelectric sublattice model (Sawada *et al* 1975; Kopsky 1976) and one involving changes in hydrogen bonding (Schlemper and Hamilton 1966) have been proposed to explain the mechanism of phase transition in this crystal. However, a fully satisfactory theoretical model explaining all the observed features is still lacking for reasons discussed below.

The order-disorder model as proposed by O'Reilly and Tsang by deutron resonance technique attributes the transition to a disordering of NH_4^+ ions with respect to the *ab* plane in the paraelectric phase. Schlemper and Hamilton have found by neutron diffraction methods, that the strength of hydrogen bonds were different in the two phases and hence the change in the H-bond scheme could be a triggering mecha-

nism. Sawada *et al* (1973) have proposed a phenomenological soft mode theory to explain the small Curie constant and other thermodynamical quantities of $(NH_4)_2SO_4$. The theory is based on the assumption that the phase transition is associated with two normal coordinates which are given by the superposition of a polar-translational symmetry coordinate and a nonpolar vibrational one. The softening of the normal mode with a large component of the vibrational mode induces the phase transition. However no such soft mode has been found as yet in the infrared absorption measurements (Torrie *et al* 1972). Sawada *et al* (1975), have studied the role of NH_4^+ ions by measuring the spontaneous polarization and the dielectric constant in $[(NH_4)_{1-x}K_x]_2SO_4$ for various values of x and proposed a two non-equivalent sublattice model to explain the phenomena. Neutron scattering measurements of mixed crystals of ammonium sulphate and potassium sulphate have been carried out (Goyal and Dasannacharya 1978). Spin lattice relaxation time of proton measurements have been carried out in $(NH_4)_2SO_4$-K_2SO_4 mixed crystals (Masaru Kasahara *et al* 1975). It has been found that potassium ions prefer to occupy the $(NH_4)_I^+$ sites rather than $(NH_4)_{II}^+$ sites and only one type of NH_4^+ ions, namely $(NH_4)_{II}^+$ remains at higher concentrations of K_2SO_4. X-ray crystal studies of the mixed system of $(NH_4)_2SO_4$-K_2SO_4 have been done (Yochi Shiozaki *et al* 1977). Abe *et al* (1978) have studied the ESR of pure and mixed crystals of ammonium and potassium sulphate. Substitution of $(NH_4)_I^+$ by potassium lowers the value of P_s and deuteration does not alter significantly the T_c. A recent ESR study of radiation damaged $(NH_4)_2SO_4$ crystal doped with CrO_4 in our laboratory suggests that a distortion of the (SO_4) groups in the low temperature phase could also be a transition parameter (Misra 1982).

As the laser Raman spectra of the $[(NH_4)_{1-x}K_x]_2SO_4$ can throw light on the extent of deformation of the SO_4^{2-} and NH_4^+ groups in different phases and the consequent changes in the N-H ... O bond strengths, the present study was made.

2. Experimental

$(NH_4)_2SO_4$ forms a continuous series of mixed crystals $[(NH_4)_{1-x}K_x]_2SO_4$ with K_2SO_4. Single crystals of various concentrations of K ($x = 0{\cdot}03$, $0{\cdot}06$, $0{\cdot}11$, $0{\cdot}28$, $0{\cdot}5$, $0{\cdot}6$ and $0{\cdot}85$) were grown by a slow evaporation of an aqueous solution at room temperature. The values of x in the crystals were determined by using the data of Bovalini and Fabris (Seidel 1965). Infrared spectra and powder x-ray diffraction pictures were used to identify the crystals.

Raman spectra were recorded with a Spex-Ramalog-6 spectrometer. The spectral slitwidth was set to 1–2 cm^{-1} band pass. Detection was by a photon-counting system using a RCA (C31034) photomultiplier with Ga-As photocathode and with thermoelectric cooling. The IR absorption spectra of the crystal were recorded using a Perkin Elmer 580 IR spectrophotometer and KBr pellet method.

The sample was illuminated with 4880 Å radiation of Ar^+ ion laser with power output in the range 100–200 mW. The temperature of the sample was varied using a simple continuous flow cryostat and the temperature stability was $\pm$ 1K.

The x-ray (Ogg and Hopwood 1916; Ogg 1928, 1930; Tutton 1930; Taylor and Boyer 1928), electron diffraction (Dalova and Pinsker 1964) and neutron diffraction

studies (Schlemper and Hamilton 1966) show that the structure has the space group D_{2h}^{16} in the paraelectric phase and C_{2v}^{9} in the ferroelectric phase and there are four molecules per unit cell. The sulphur atoms, two oxygen atoms, the nitrogen atoms and four hydrogen atoms lie in the mirror plane (001). Hence NH_4^+ and SO_4^{2-} ions occupy sites of symmetry C_s in the high temperature phase and C_1 symmetry in the low temperature phase.

The polarizability tensor components associated with the Raman active modes are α_{xx}, α_{yy} and α_{zz} for Ag, α_{xy} for B_{1g}, α_{xz} for B_{2g} and α_{yz} for B_{3g}. Raman spectra of mixed crystals of ammonium sulphate and potassium sulphate were taken for six orientations at room temperature 293 K.

3. Results and discussion

Raman spectra of $[(NH_4)_{1-x}K_x]_2SO_4$ were taken at room temperature 293 K for concentrations, $x = 0$, 0·03, 0·06, 0·11, 0·28, 0·5 and 0·6 for six orientations. The frequencies and the assignments of the various bands are given for $[(NH_4)_{0.97}K_{0.03}]_2SO_4$ in table 1 and the correlation diagram for this crystal in the para and ferroelectric phases are given in tables 2 and 3 respectively. In the paraelectric phase, all the gerade components are Raman active and the ungerade components excepting A_u

Table 1. Frequencies and assignment of single crystal Raman spectra of paraelectric $[(NH_4)_{0.97}K_{0.03}]_2SO_4$.

Frequency (cm^{-1})	Symmetry	Assignment	Frequency (cm^{-1})	Symmetry	Assignment
41	A_g		624	A_g	
60	B_{1g}	SO_4^{2-} translation	637	B_{1g}	
68	B_{3g}		976	A_g	SO_4^{2-} ν_1 vibration
71	B_{2g}		976	B_{1g}	
76	A_g	SO_4^{2-} libration	1065	A_g	SO_4^{2-} ν_3 vibration
82	B_{1g}		1074	B_{1g}	
90	B_{2g}		1087	B_{3g}	
152	B_{2g}		1090	B_{2g}	
184	A_g	NH_4^+ translation	1102	A_g	
193			1120	B_{1g}	
358	B_{3g}	NH_4^+ libration	1413	A_g	
375	A_g		1419	B_{1g}	NH_4^+ ν_4 vibration
451	A_g		1424	B_{3g}	
451	B_{1g}	SO_4^{2-} ν_2 vibration	1660	A_g	
454	B_{2g}		1665	B_{2g}	NH_4^+ ν_2 vibration
453	B_{3g}		1670	B_{1g}	
612	A_g		1690	B_{3g}	
615	B_{3g}	SO_4^{2-} ν_4 vibration	3030	B_{1g}	NH_4^+ ν_1 vibration
618	B_{1g}		3150	A_g	NH_4^+ ν_3 vibration
618	B_{2g}		3175		
			3290		

Table 2. Symmetry correlation for paraelectric $(NH_4)_2SO_4$ in the room temperature 293 K.

Free Ion T_d	Site C_s	Crystal D_{2h}	Activity
A_1	A'	A_g	Raman
E		B_{1g}	Raman
		B_{2g}	Raman
F_1	A''	B_{3g}	Raman
		A_u	Inactive
F_2		B_{1u}	I.R.
		B_{2u}	I.R.
		B_{3u}	I.R.

Table 3. Correlation diagram for $(NH_4)_2SO_4$ in the ferroelectric phase (below $T_c = 223°$ K).

Free Ion T_d	Site C_1	Crystal C_{2v}	Activity
A_1	A	A_1	Raman and IR
E		A_2	Raman
F_1		B_1	Raman and IR
F_2		B_2	Raman and IR

are active in IR. In the ferroelectric phase the atoms occupy only general positions. As the concentration x of K^+ ions increases in the mixed crystal up to 50%, the frequencies of totally symmetric vibration (ν_1) of SO_4^{2-} and NH_4^+ increase, while that of antisymmetric vibrations of NH_4^+ decrease which is shown in figure 1 (a, b). The infrared spectra of mixed crystals at different concentrations of K^+ ions are shown in figure 2. The crystal structure of ammonium sulphate at 293 K is shown in figure 3. The ammonium sulphate structure consists of one type of SO_4^{2-} group and two types of NH_4^+ groups, namely $(NH_4)_I^+$ and $(NH_4)_{II}^+$. One hydrogen from each type of ammonium is coupled to the sulphate group through the oxygens O(1) and O(2) which lie in the *ab* mirror plane. From NMR results, it is seen that the potassium prefers to occupy only $(NH_4)_I^+$ site. Therefore, if a K^+ ion replaces one of the $(NH_4)_I^+$ ion, the charge distribution of SO_4^{2-} ion is modified because of the disappearance of the hydrogen bond. The change in the charge distribution of SO_4^{2-} ion affects the state of the remaining hydrogen bonds. Therefore the strength of S-O bond increases and hence the frequency of the totally symmetric SO_4^{2-} vibrations increases. This continues until all the $(NH_4)_I^+$ ions are replaced by K^+. From figure 4, it can be seen that up to a concentration of 50% of potassium the frequency increases and thereafter it decreases up to 60%. Then the frequency increases and attains the value of 983 cm^{-1} which is that of K_2SO_4. The increase in (ν_1) frequency of SO_4^{2-} vibrations up to 50% of potassium is due to the disappearance of more and more hydrogen bonds. Once the concentration of K^+ ions is greater than 50%, all the hydrogen bonds are broken

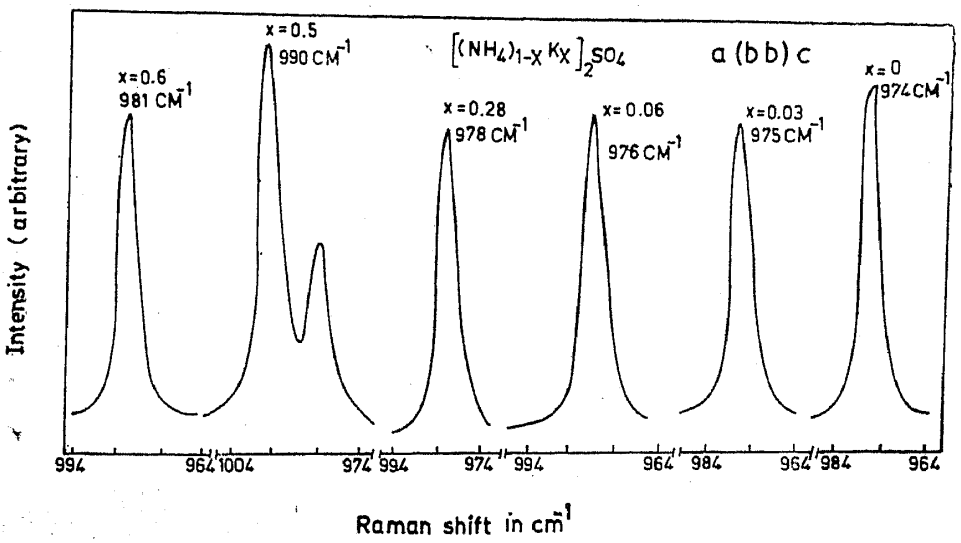


Figure 1a. Raman spectra of totally symmetric frequency (ν_1) of $(SO_4)^{2-}$ vibrations.

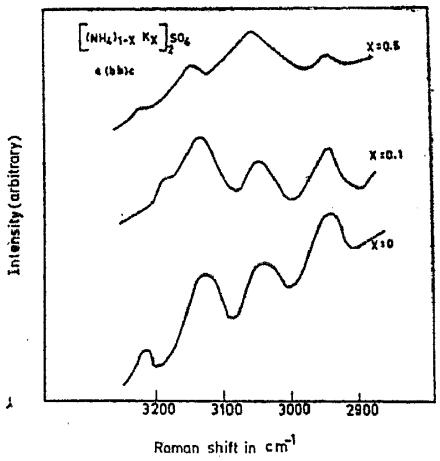


Figure 1b. The NH_4^+ stretch frequency with the different concentrations of potassium in $(NH_4)_2SO_4$-K_2SO_4 mixed crystals.

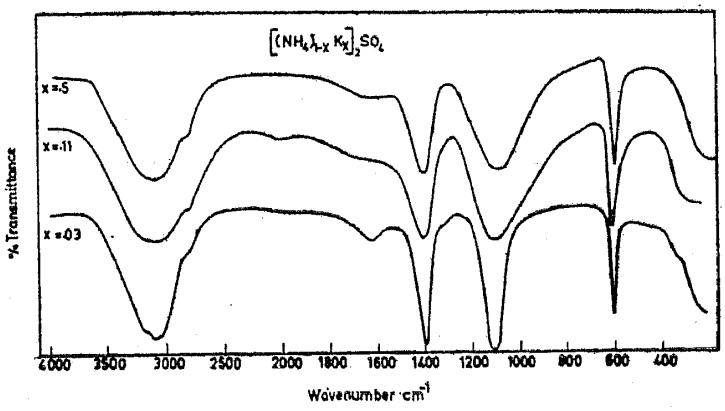


Figure 2. Infrared spectra of $[(NH_4)_{1-x}K_x]_2SO_4$ in various concentrations at 298 K.

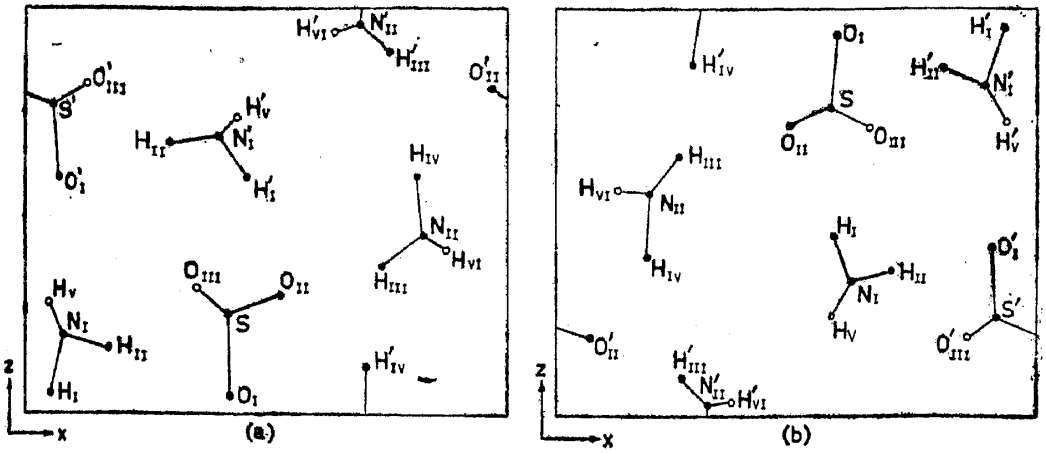


Figure 3. Sketch of structure of ammonium sulphate in the room temperature. (a) Projections on the plane $y = \frac{1}{4}$ of atoms which lie between the planes $y = 0$ and $y = \frac{1}{2}$; (b) Projection on the plane $y = \frac{3}{4}$ of atoms which lie between the planes $y = \frac{1}{2}$ and $y = 1$.

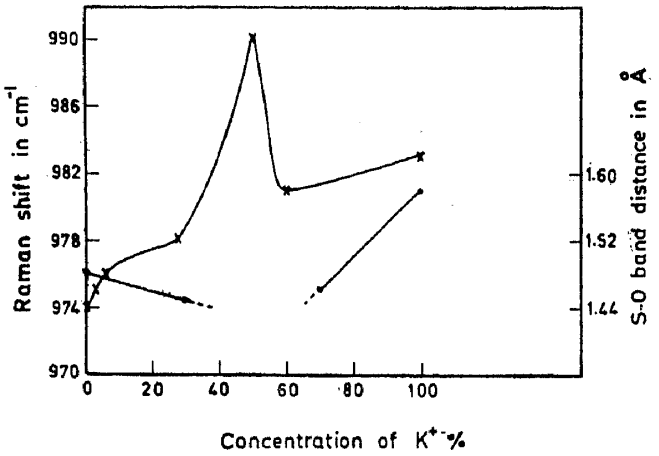


Figure 4. Variation of totally symmetric frequency ν_1 of $(SO_4)^{2-}$ vibration as a function of concentration of potassium in the mixed crystal.

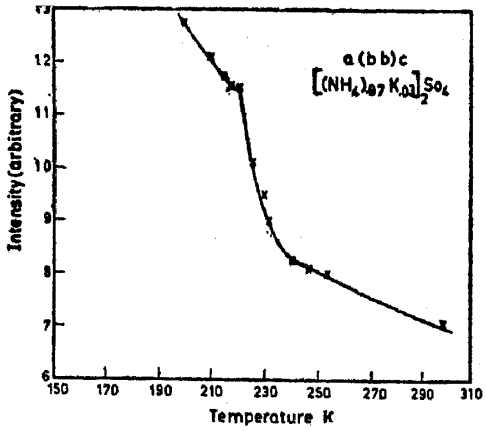


Figure 5. Intensity variation of totally symmetric frequency ν_1 of $(SO_4)^{2-}$ vibration as a function of temperature in $[(NH_4)_{0\cdot97}\ K_{0\cdot03}]_2SO_4$.

and the vibrations of the SO_4^{2-} groups are similar to that in K_2SO_4. The frequency of the totally symmetric vibration falls down up to 60% of K^+ and thereafter it in-

creases gradually and reaches 983 cm^{-1} which is the frequency of the totally symmetrical frequency (ν_1) of SO_4^{2-} vibration in K_2SO_4. X-ray studies on the mixed crystals of $(NH_4)KSO_4$ also show this behaviour where S-O distance decreases first up to 30% and from 70% of K^+ concentration, it increases. The region between 30% and 60% of K^+ concentration may be the critical region in which the hydrogen bond effect and ionic radii consideration compete with each other.

When the crystal containing 3% of K^+ is cooled to the ferroelectric phase, the intensity of totally symmetric vibration (ν_1) of SO_4^{2-} increases gradually and near the phase transition temperature 223 K, there is a steep increase in intensity and the slope of the line changes rather abruptly. As the concentration of K^+ is increased to 11% and 50%, there is a gradual increase in intensity of this vibration and the change of slope with temperature becomes smooth (figures 5, 6 and 7). The transition temperature is found to shift from 221 K for $[(NH_4)_{0.97}\ K_{0.03}]_2\ SO_4$ crystal to 216 K and 165 K for crystals containing 11% and 50% of potassium sulphate. When the concentration

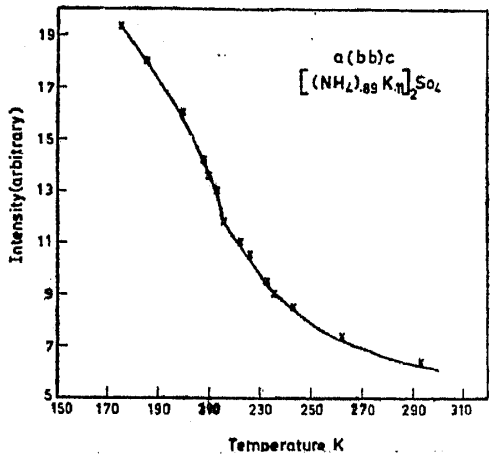


Figure 6. Same as figure 5 in $[(NH_4)_{0\cdot89}\ K_{0\cdot11}]_2SO_4$.

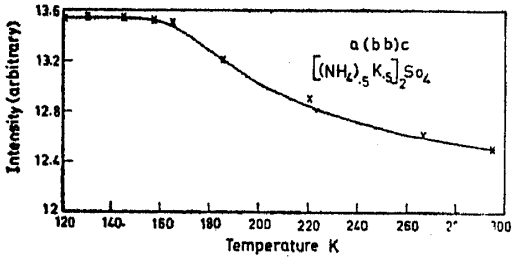


Figure 7. Same as figure 5 in $[(NH_4)_{0\cdot5}\ K_{0\cdot5}]_2SO_4$.

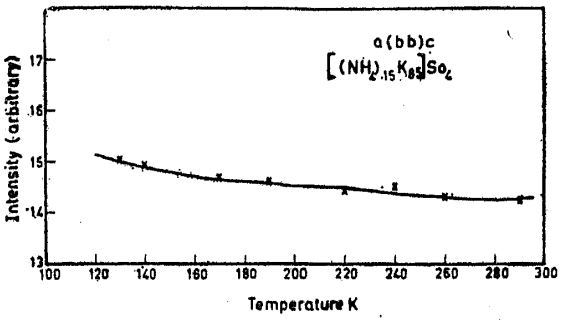
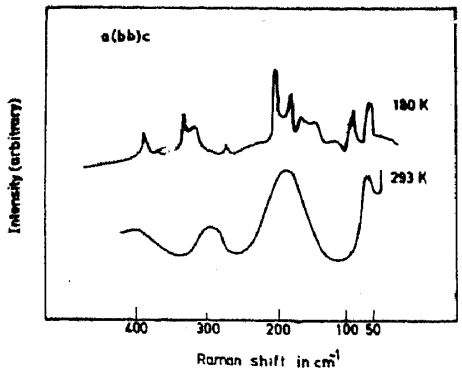


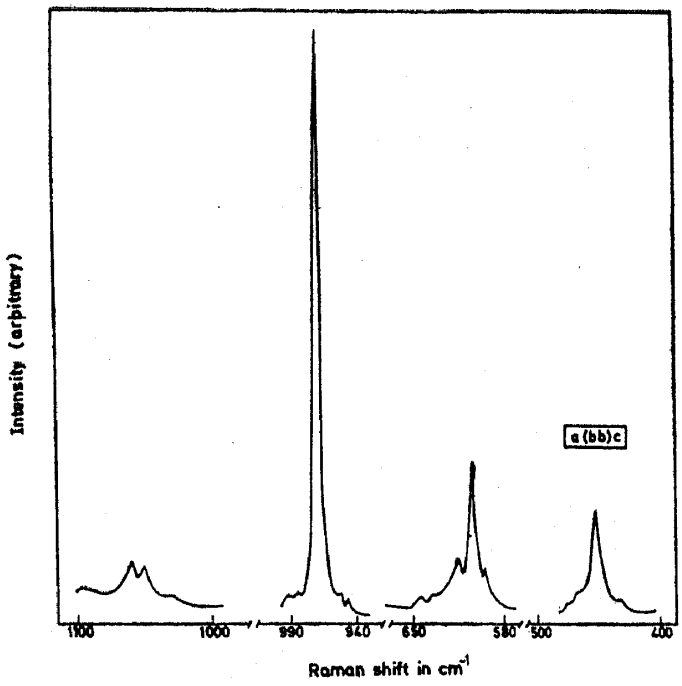
Figure 7a. Same as figure 5 in $[(NH_4)_{0\cdot15}\ K_{0\cdot85}]_2SO_4$.

of K^+ ions increases, in the mixed crystal, the transition is found to change from a first order type to one of second order, as is seen from the variation of the slope of the intensity of ν_1 line of SO_4^{2-} vibrations with temperature. For the crystal containing 85% of potassium, there is no phase transition, as the intensity almost linearly increases with temperature (figure 7a). This result is in conformity with the dielectric studies of mixed crystals (Sawada 1975).

In the lattice region of the spectra of $(NH_4)_2SO_4$ and other mixed crystals, the lines become sharp at low temperature but no sudden changes either in intensity or frequencies are observed. Typical Raman spectra of $(NH_4)_2SO_4$ at 293 K and low temperatures are shown in figure 8 (a, b). However, the ν_4 mode of sulphate at 614 cm^{-1} in $(NH_4)_2SO_4$ gives rise to 612, 618, 627 and 637 cm^{-1} respectively in the ferroelectric phase (figure 9). This result is similar to the one observed for ν_3 line of $(SO_4)^{2-}$ where



8a.



8b.

Figure 8a. Typical Raman spectra of pure $(NH_4)_2SO_4$ at 293 and 180 K in the spectral region 50–400 cm^{-1}. b. in the spectral region 400–1100 cm^{-1} at 293 K.

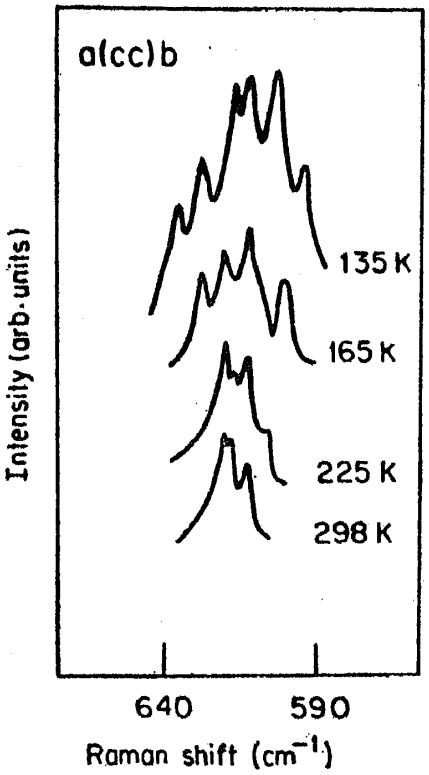


Figure 9. Variation of ν_4 mode of $(SO_4)^{2-}$ as a function of temperature.

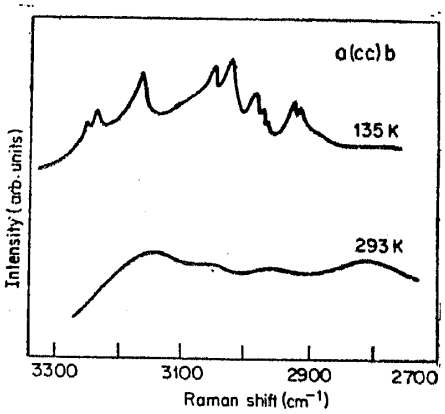


Figure 10. Raman spectra of $(NH)_4^+$ stretch frequency region at 293 and 135 K.

the SO_4^{2-} ion is said to be distorted in the ferroelectric phase (Iqbal and Christoe 1976). No sudden change in intensity or width or frequency is observed in the N-H bond region of this crystal excepting a general narrowing of the band as the temperature is lowered (figure 10). The totally symmetric line (ν_1) at 976 cm^{-1} decreases to 973 cm^{-1} in $(NH_4)_2SO_4$ as the crystal is cooled below T_c, which means that the strength of hydrogen bond increases.

4. Conclusion

From the above results, it can be inferred that the phase transition in mixed crystals of $[(NH_4)_{1-x}\ K_x]_2\ SO_4$ is not simply due to the order-disorder of (NH_4) radicals or

due to hydrogen bonding alone but due to the cooperative phenomena of the coupling between $(NH_4)^+$ ions through hydrogen bonds with the distorted SO_4^{2-} ions in the low temperature phase.

Acknowledgements

One of the authors (vs) wishes to express his thanks to Prof. R Srinivasan, for his keen interest in this work. He is also thankful to Prof. C N R Rao, for getting the infrared absorption spectra of the crystals. He is grateful to the University Grants Commission, New Delhi for the award of Teacher Fellowship under the faculty improvement programme.

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