

## Laser Raman spectra of mixed crystals of $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$

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**Abstract.** The Raman spectra of mixed crystals of  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  in the region 50-3400  $\text{cm}^{-1}$  at 293 K and below 223 K have been reported. At room temperature 293 K, as the concentration of  $\text{K}^+$  ion increases in the crystal up to 50%, the frequencies of the totally symmetric vibrations of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  ions increase and thereafter the frequency of  $\text{SO}_4^{2-}$  vibration decreases and attains the value in  $\text{K}_2\text{SO}_4$ . 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  $A_g(\nu_1)$  mode of  $\text{SO}_4^{2-}$  for various concentrations ( $x = 0, 0.03, 0.11, 0.5, 0.85$ ) suggest that the phase transition changes from first order type to one of second order. The phase transition in mixed crystals of  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  can be a cooperative phenomenon arising from a coupling between  $(\text{NH}_4)^+$  ions through hydrogen bonds with the distorted  $\text{SO}_4^{2-}$  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  $Q = 0.93$  kcal/mole,  $S = 4.2$  cal/mole/deg (Hoshino *et al* 1958). The crystal exhibits an anomalous change in polarization; a very low value of Curie-Weiss constant ( $\sim 15$  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 neutron resonance technique attributes the transition to a disordering of  $\text{NH}_4^+$  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  $(\text{NH}_4)_2\text{SO}_4$ . 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  $\text{NH}_4^+$  ions by measuring the spontaneous polarization and the dielectric constant in  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  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  $(\text{NH}_4)_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  mixed crystals (Masaru Kasahara *et al* 1975). It has been found that potassium ions prefer to occupy the  $(\text{NH}_4)_I^+$  sites rather than  $(\text{NH}_4)_{II}^+$  sites and only one type of  $\text{NH}_4^+$  ions, namely  $(\text{NH}_4)_{II}^+$  remains at higher concentrations of  $\text{K}_2\text{SO}_4$ . X-ray crystal studies of the mixed system of  $(\text{NH}_4)_2\text{SO}_4$  -  $\text{K}_2\text{SO}_4$  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  $(\text{NH}_4)_I^+$  by potassium lowers the value of  $P_s$  and deuteration does not alter significantly the  $T_c$ . A recent ESR study of radiation damaged  $(\text{NH}_4)_2\text{SO}_4$  crystal doped with  $\text{CrO}_4$  in our laboratory suggests that a distortion of the  $(\text{SO}_4)$  groups in the low temperature phase could also be a transition parameter (Misra 1982).

As the laser Raman spectra of the  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  can throw light on the extent of deformation of the  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  groups in different phases and the consequent changes in the N-H ... O bond strengths, the present study was made.

## 2. Experimental

$(\text{NH}_4)_2\text{SO}_4$  forms a continuous series of mixed crystals  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  with  $\text{K}_2\text{SO}_4$ . Single crystals of various concentrations of K ( $x = 0.03, 0.06, 0.11, 0.28, 0.5, 0.6$  and  $0.85$ ) 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  $1-2 \text{ cm}^{-1}$  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  $4880 \text{ \AA}$  radiation of  $\text{Ar}^+$  ion laser with power output in the range  $100-200 \text{ mW}$ . The temperature of the sample was varied using a simple continuous flow cryostat and the temperature stability was  $\pm 1 \text{ K}$ .

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  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  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  $\alpha_{xx}$ ,  $\alpha_{yy}$  and  $\alpha_{zz}$  for  $A_g$ ,  $\alpha_{xy}$  for  $B_{1g}$ ,  $\alpha_{xz}$  for  $B_{2g}$  and  $\alpha_{yz}$  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  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  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  $[(\text{NH}_4)_{0.97}\text{K}_{0.03}]_2\text{SO}_4$  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  $[(\text{NH}_4)_{0.97}\text{K}_{0.03}]_2\text{SO}_4$ .

Frequency ( $\text{cm}^{-1}$ )	Symmetry	Assignment	Frequency ( $\text{cm}^{-1}$ )	Symmetry	Assignment
41	$A_g$		624	$A_g$	
60	$B_{1g}$	$\text{SO}_4^{2-}$ translation	637	$B_{1g}$	
68	$B_{3g}$		976	$A_g$	$\text{SO}_4^{2-}$ $\nu_1$ vibration
71	$B_{2g}$		976	$B_{1g}$	
76	$A_g$	$\text{SO}_4^{2-}$ libration	1065	$A_g$	$\text{SO}_4^{2-}$ $\nu_3$ vibration
82	$B_{1g}$		1074	$B_{1g}$	
90	$B_{2g}$		1087	$B_{3g}$	
152	$B_{2g}$		1090	$B_{2g}$	
184	$A_g$	$\text{NH}_4^+$ translation	1102	$A_g$	
193			1120	$B_{1g}$	
358	$B_{3g}$	$\text{NH}_4^+$ libration	1413	$A_g$	
375	$A_g$		1419	$B_{1g}$	$\text{NH}_4^+$ $\nu_4$ vibration
451	$A_g$		1424	$B_{3g}$	
451	$B_{1g}$	$\text{SO}_4^{2-}$ $\nu_2$ vibration	1660	$A_g$	
454	$B_{2g}$		1665	$B_{2g}$	$\text{NH}_4^+$ $\nu_2$ vibration
453	$B_{3g}$		1670	$B_{1g}$	
612	$A_g$		1690	$B_{3g}$	
615	$B_{3g}$	$\text{SO}_4^{2-}$ $\nu_4$ vibration	3030	$B_{1g}$	$\text{NH}_4^+$ $\nu_1$ vibration
618	$B_{1g}$		3150	$A_g$	$\text{NH}_4^+$ $\nu_3$ vibration
618	$B_{2g}$		3175		
			3290		

**Table 2.** Symmetry correlation for paraelectric  $(\text{NH}_4)_2\text{SO}_4$  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
$F_1$	$A''$	$B_{2g}$	Raman
$F_2$		$B_{3g}$	Raman
		$A_u$	Inactive
		$B_{1u}$	I.R.
		$B_{2u}$	I.R.
		$B_{3u}$	I.R.

**Table 3.** Correlation diagram for  $(\text{NH}_4)_2\text{SO}_4$  in the ferroelectric phase (below  $T_c = 223^\circ \text{K}$ ).

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  $\text{K}^+$  ions increases in the mixed crystal up to 50%, the frequencies of totally symmetric vibration ( $\nu_1$ ) of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  increase, while that of antisymmetric vibrations of  $\text{NH}_4^+$  decrease which is shown in figure 1 (a, b). The infrared spectra of mixed crystals at different concentrations of  $\text{K}^+$  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  $\text{SO}_4^{2-}$  group and two types of  $\text{NH}_4^+$  groups, namely  $(\text{NH}_4)_I^+$  and  $(\text{NH}_4)_{II}^+$ . 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  $(\text{NH}_4)_I^+$  site. Therefore, if a  $\text{K}^+$  ion replaces one of the  $(\text{NH}_4)_I^+$  ion, the charge distribution of  $\text{SO}_4^{2-}$  ion is modified because of the disappearance of the hydrogen bond. The change in the charge distribution of  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  vibrations increases. This continues until all the  $(\text{NH}_4)_I^+$  ions are replaced by  $\text{K}^+$ . 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  $983 \text{ cm}^{-1}$  which is that of  $\text{K}_2\text{SO}_4$ . The increase in ( $\nu_1$ ) frequency of  $\text{SO}_4^{2-}$  vibrations up to 50% of potassium is due to the disappearance of more and more hydrogen bonds. Once the concentration of  $\text{K}^+$  ions is greater than 50%, all the hydrogen bonds are broken

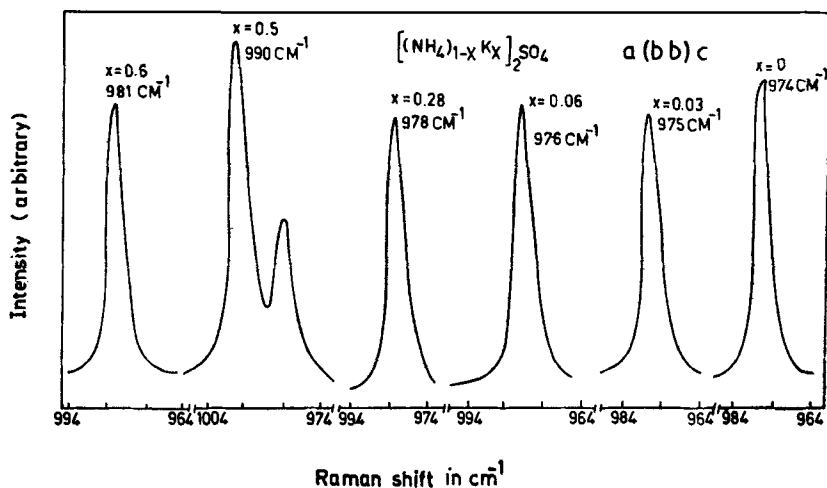


Figure 1a. Raman spectra of totally symmetric frequency ( $\nu_1$ ) of  $(\text{SO}_4)^{2-}$  vibrations.

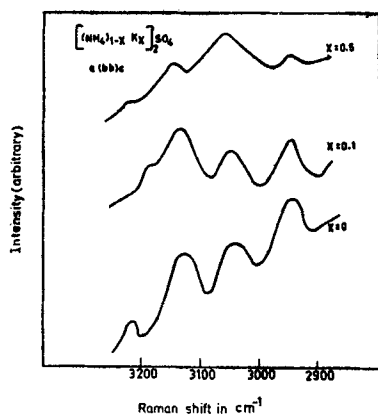


Figure 1b. The  $\text{NH}_4^+$  stretch frequency with the different concentrations of potassium in  $(\text{NH}_4)_2\text{SO}_4$ - $\text{K}_2\text{SO}_4$  mixed crystals.

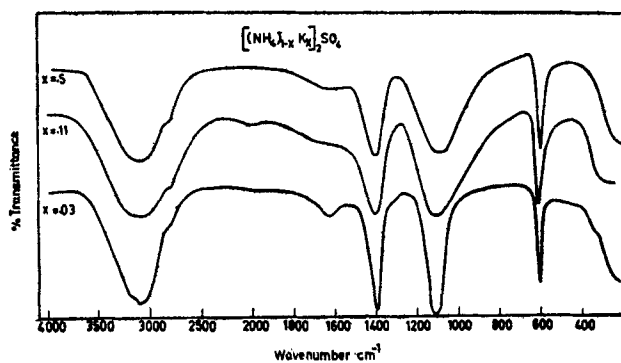


Figure 2. Infrared spectra of  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  in various concentrations at 298 K.

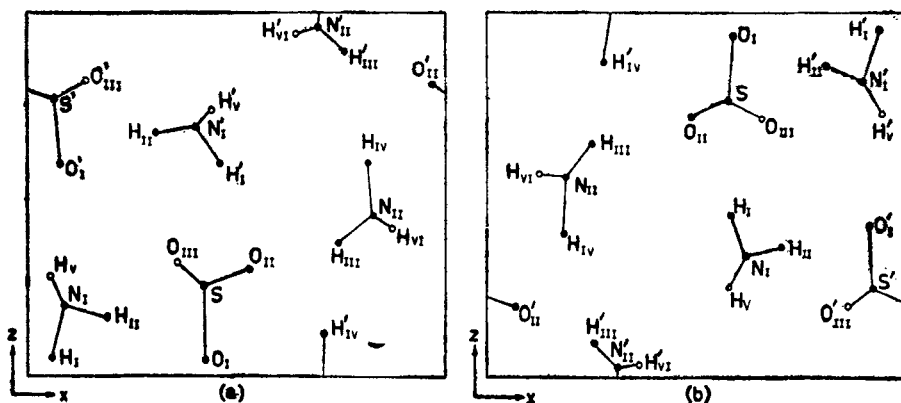


Figure 3. Sketch of structure of ammonium sulphate in the room temperature. (a) Projections on the plane  $y = \frac{1}{2}$  of atoms which lie between the planes  $y = 0$  and  $y = \frac{1}{2}$ ; (b) Projection on the plane  $y = \frac{1}{2}$  of atoms which lie between the planes  $y = \frac{1}{2}$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

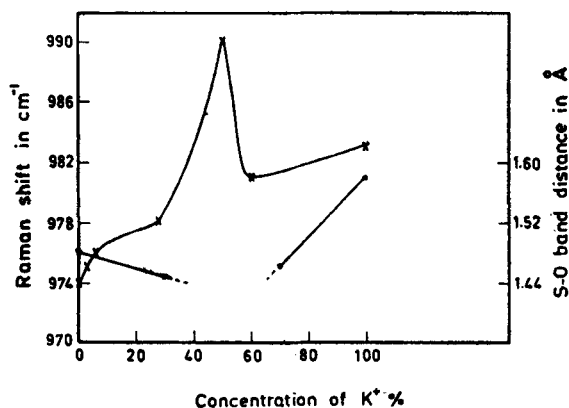


Figure 4. Variation of totally symmetric frequency  $\nu_1$  of  $(\text{SO}_4)^{2-}$  vibration as a function of concentration of potassium in the mixed crystal.

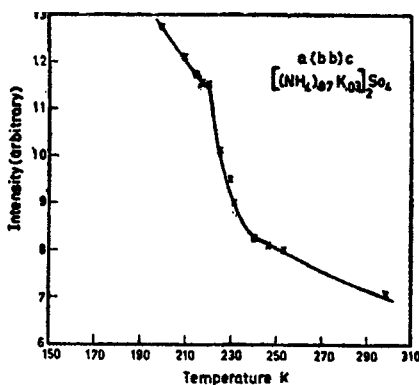


Figure 5. Intensity variation of totally symmetric frequency  $\nu_1$  of  $(\text{SO}_4)^{2-}$  vibration as a function of temperature in  $[(\text{NH}_4)_{0.97} \text{K}_{0.03}]_2 \text{SO}_4$ .

and the vibrations of the  $\text{SO}_4^{2-}$  groups are similar to that in  $\text{K}_2\text{SO}_4$ . The frequency of the totally symmetric vibration falls down up to 60% of  $\text{K}^+$  and thereafter it in-

creases gradually and reaches  $983\text{ cm}^{-1}$  which is the frequency of the totally symmetrical frequency ( $\nu_1$ ) of  $\text{SO}_4^{2-}$  vibration in  $\text{K}_2\text{SO}_4$ . X-ray studies on the mixed crystals of  $(\text{NH}_4)\text{KSO}_4$  also show this behaviour where S-O distance decreases first up to 30% and from 70% of  $\text{K}^+$  concentration, it increases. The region between 30% and 60% of  $\text{K}^+$  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  $\text{K}^+$  is cooled to the ferroelectric phase, the intensity of totally symmetric vibration ( $\nu_1$ ) of  $\text{SO}_4^{2-}$  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  $\text{K}^+$  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  $[(\text{NH}_4)_{0.97}\text{K}_{0.03}]_2\text{SO}_4$  crystal to 216 K and 165 K for crystals containing 11% and 50% of potassium sulphate. When the concentration

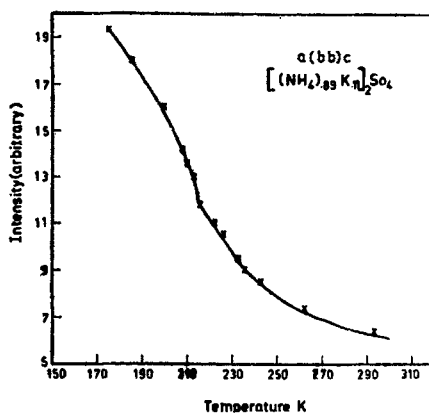


Figure 6. Same as figure 5 in  $[(\text{NH}_4)_{0.99}\text{K}_{0.11}]_2\text{SO}_4$ .

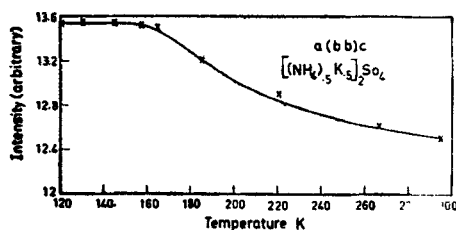


Figure 7. Same as figure 5 in  $[(\text{NH}_4)_{0.5}\text{K}_{0.5}]_2\text{SO}_4$ .

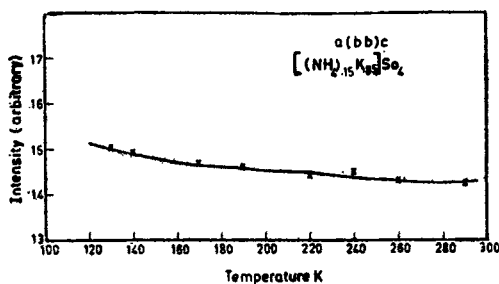
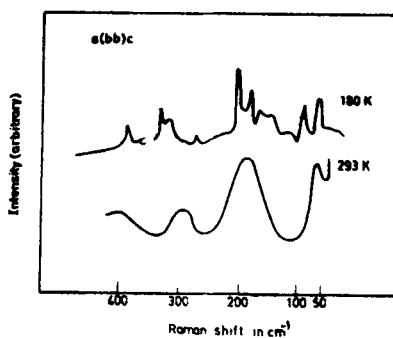


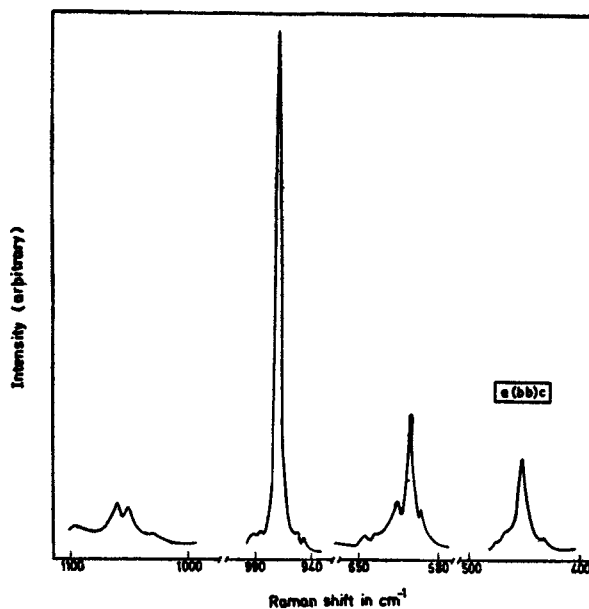
Figure 7a. Same as figure 5 in  $[(\text{NH}_4)_{0.15}\text{K}_{0.85}]_2\text{SO}_4$ .

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  $\nu_1$  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  $\nu_4$  mode of sulphate at  $614\text{ cm}^{-1}$  in  $(NH_4)_2SO_4$  gives rise to  $612, 618, 627$  and  $637\text{ cm}^{-1}$  respectively in the ferroelectric phase (figure 9). This result is similar to the one observed for  $\nu_3$  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  $50\text{--}400\text{ cm}^{-1}$ . b. in the spectral region  $400\text{--}1100\text{ cm}^{-1}$  at 293 K.



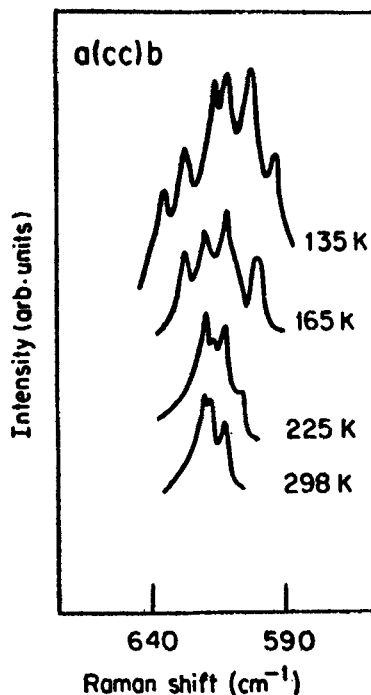


Figure 9. Variation of  $\nu_4$  mode of  $(\text{SO}_4)^{2-}$  as a function of temperature.

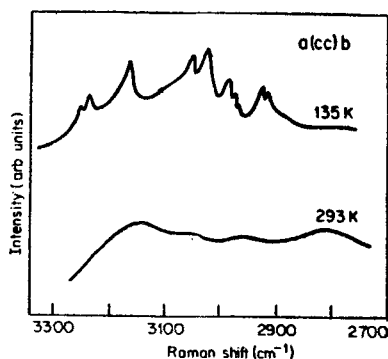


Figure 10. Raman spectra of  $(\text{NH}_4)^+$  stretch frequency region at 293 and 135 K.

the  $\text{SO}_4^{2-}$  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 ( $\nu_1$ ) at  $976 \text{ cm}^{-1}$  decreases to  $973 \text{ cm}^{-1}$  in  $(\text{NH}_4)_2\text{SO}_4$  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  $[(\text{NH}_4)_{1-x}\text{K}_x]_2\text{SO}_4$  is not simply due to the order-disorder of  $(\text{NH}_4)$  radicals or

due to hydrogen bonding alone but due to the cooperative phenomena of the coupling between  $(\text{NH}_4)^+$  ions through hydrogen bonds with the distorted  $\text{SO}_4^{2-}$  ions in the low temperature phase.

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