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Raman studies of the 223 K phase transition in $(NH_4)_2SO_4$ single crystal

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Abstract. The temperature dependence of the $z(yy)x$ Raman spectrum was studied in $(NH_4)_2SO_2$ single crystal in the temperature range 300–100 K. The temperature dependence of the NH_4 translational Raman bands in the region of 200 cm^{-1} seems to support the hypothesis that the peculiar temperature dependence of the spontaneous polarization in $(NH_4)_2SO_4$ single crystal may be ascribed to the competing polarization contributions from the NH_4^+ (I) and NH_4^+ (II) dipoles of opposite direction with differing reorientational relaxation temperature dependences, and also the NH_4^+–SO_4^{2-} displacive lattice polarization, which was neglected in the point-charge model.

1. Introduction

Ammonium sulphate ($(NH_4)_2SO_4$, hereafter abbreviated as AS) single crystal has a phase transition at $T_c = 223$ K and is classified as an improper ferroelectric (Kobayashi et al 1972) or a pseudo-proper ferroelectric (Petzelt et al 1974).

The spontaneous polarization P_s of AS single crystal shows a peculiar temperature dependence (Unruh 1970). Although some attempts were made to explain the spontaneous polarization of AS single crystal, such as the point-charge model calculation (Jain and Bist 1974) and the ferrielectric ordering involving nonequivalent NH_4^+(I) and NH_4^+(II) ions of two crystallographically different sublattices (Sawada 1975), essential details remain unknown to understand, for example, how the two NH_4^+(I) and NH_4^+(II) groups contribute to the spontaneous polarization P_s. The spontaneous polarization P_s is certainly not the order parameter of the phase transition in AS single crystal; however, reorientation of NH_4^+ ions (O'Reilly and Tsang 1967a,b,c, Petzelt et al 1974, Kozlov et al 1988), molecular distortion of SO_4^{2-} ions (Jain et al 1986, Bajpai and Jain 1987), etc, have been proposed as the order parameter. Petzelt et al (1974) first offered the explanation of the spontaneous polarization in terms of the coupled oscillator-relaxator model where the translational motion of NH_4^+ ion coulped with hindered rotation was proposed as responsible for the peculiar spontaneous polarization P_s. This far infrared study of Petzelt et al (1974) in the region of 200 cm^{-1} has not been reexamined by works using Raman techniques, although many Raman scattering studies of AS single crystal dealing with many other aspects have been reported (Torrie et al 1972, Iqbal and Christoe 1976, Unruh et al 1978a,b).

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We have studied in considerable detail the temperature dependence of the Raman band of the NH_4^+ translational mode at around 200 cm^{-1}, which was suggested by Petzelt *et al* (1974) on the basis of their far infrared spectral data as being responsible for the peculiar temperature dependence of the spontaneous polarization P_s.

2. Experimental procedure

An argon–krypton mixed gas laser operated at 4880 Å with output power 80 mW, a double grating spectrometer, photon counting electronics and a closed-cycle helium refrigerator (Displex) system were employed in the present work of low-temperature Raman scattering. Raman samples were single crystals of ammonium sulphate and partially deuterated ammonium sulphate. The crystals were grown from a saturated solution at 30 °C over two weeks to obtain transparent single crystals of approximate size $(1 \times 1 \times 3)$ cm^3. The crystals were cut and surface polished to produce Raman samples of approximate size $(1 \times 1 \times 3)$ mm^3 in order to minimize the effects of 'powdery shattering' below T_c experienced with larger size samples. The partially deuterated samples were grown from a saturated solution of $(NH_4)_2SO_4$ in D_2O. The concentration x of ND_4^+ was estimated to be approximately $x = 0.65$ on the basis of the Raman intensity ratio of the NH_4^+ stretching band at 3140 cm^{-1} and the ND_4^+ stretching band at 2300 cm^{-1}. Temperature stability during experimental runs was maintained at better than ± 0.1 K near T_c, as measured by a gold (0.7% Fe)–chromel thermocouple.

3. Results and discussion

Ammonium sulphate single crystal shows three groups of Raman bands in the low-frequency region below 450 cm^{-1}: SO_4^{2-} external modes in the region below 160 cm^{-1}, NH_4^+ translational modes in the region between 160 cm^{-1} and 250 cm^{-1} and NH_4^+ librational modes in the region 250–430 cm^{-1}, as classified by Torrie *et al* (1972) on the basis of the deuteration effects on the frequency shift. The SO_4^{2-} bands observed above T_c are mostly translational modes since the distortion of SO_4^{2-} from T_d symmetry is very weak in the para-electric phase and the F_1 librational modes of T_d symmetry are Raman inactive (Venkateswarlu *et al* 1975).

In figure 1 we have shown the (yy) polarization Raman spectra of A_g/A_1 modes in the temperature range 292–102 K. The very-low-frequency SO_4^{2-} band at around 44 cm^{-1} was observed to disappear with the ferroelectric phase transition at $T_c \simeq$ 223 K, which has been suggested as being indicative of a first-order type phase transition and of the important roles played by SO_4^{2-} in the phase transition (Unruh *et al* 1978a,b). The NH_4^+ translational band, on the other hand, is seen to show a continuous change across the phase transition and the gradual band splitting occurs at temperatures well below $T_c \simeq$ 223 K, although the asymmetric broad band is better fitted by two overlapped damped oscillator bands even at room temperature. This two band structure seems to be originated from the nonequivalent $NH_4^+(I)$ and $NH_4^+(II)$ groups of the crystal as discussed in the following.

The dependence on temperature of the NH_4^+ translational band was analyzed in terms of the two damped oscillator bands using the digitized data obtained between
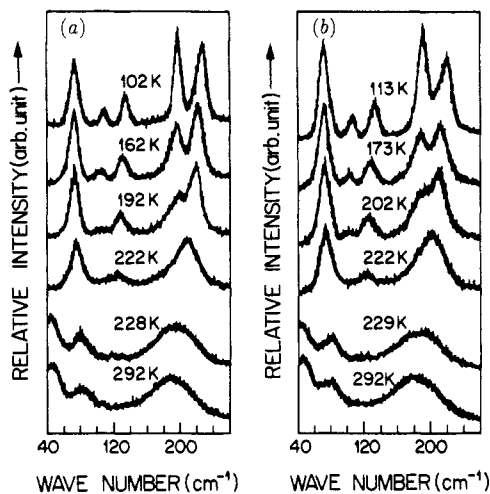
Figure 1. Temperature dependence of the lattice vibrational Raman spectra of $z(yy)x$ polarization for (a) ammonium sulphate and (b) deuterated ($\sim$ 65%) ammonium sulphate single crystals.

160 cm^{-1} and 260 cm^{-1} with the equation

$$I(\nu) = \sum_{i=1}^{2} \frac{[n(\nu) + 1]\nu S_i \Gamma_i \nu_i^2}{(\nu^2 - \nu_i^2)^2 + \nu^2 \Gamma_i^2} + I_b$$

where $I(\nu)$ is the band intensity at frequency ν, $n(\nu)$ the Bose–Einstein factor at the respective temperatures, ν_i the natural frequency of the oscillator i, Γ_i the damping constant, S_i the scattering strength of the oscillator i and I_b represents the background intensity (Loudon 1973).

Typical results of the fitting are shown in figure 2 for the 162 K band of ammonium sulphate (figure 2(a)) and the 172 K band of partially deuterated ammonium sulphate (figure 2(b)). The temperature dependences of ν_1, ν_2 and Γ_1, Γ_2 as obtained from the fitting are shown in figures 3 and 4, respectively.

For convenience in discussing our results we have drawn in figure 5 the schematic projections of the unit cell on the ab and bc planes on the basis of the 180 K neutron diffraction data of Schlemper and Hamilton (1966) and have calculated the direction cosines and the nearest-neighbour distances of the SO$_4^{2-}$ ions as shown in table 1.

From table 1 we may expect two different SO$_4^{2-}$–NH$_4^+$ translational bands to appear in the (yy) polarized Raman spectrum: a SO$_4^{2-}$–NH$_4^+$(I) band and a SO$_4^{2-}$–NH$_4^+$(II) band. Assuming the bond polarizability contribution to the Raman polarization and the stronger contributions from the nearest-neighbour bonds, we may expect the strongest contribution to the NH$_4^+$(I) band to come from the SO$_4^{2-}$–NH$_4^+$(I4) bond with $d = 3.4$ Å and $\beta = -0.99$, and to the NH$_4^+$(II) band from the SO$_4^{2-}$–NH$_4^+$(II2) with $d = 3.72$ Å and the SO$_4^{2-}$–NH$_4^+$(II$\bar{2}$) bond with $d = 3.66$ Å, where d is the S–N distance and β is the y component of the direction cosines for the S–N bond (see figure 5 and table 1). With the Coulomb potential force constant varying as d^{-3}, we expect the natural frequency ratio ν_1/ν_2 between the NH$_4^+$(I) band and the NH$_4^+$(II) band to be $(d_1/d_2)^{-3/2} \simeq (3.40/3.69)^{-3/2} \simeq 1.131$, which is close to the curve fitting
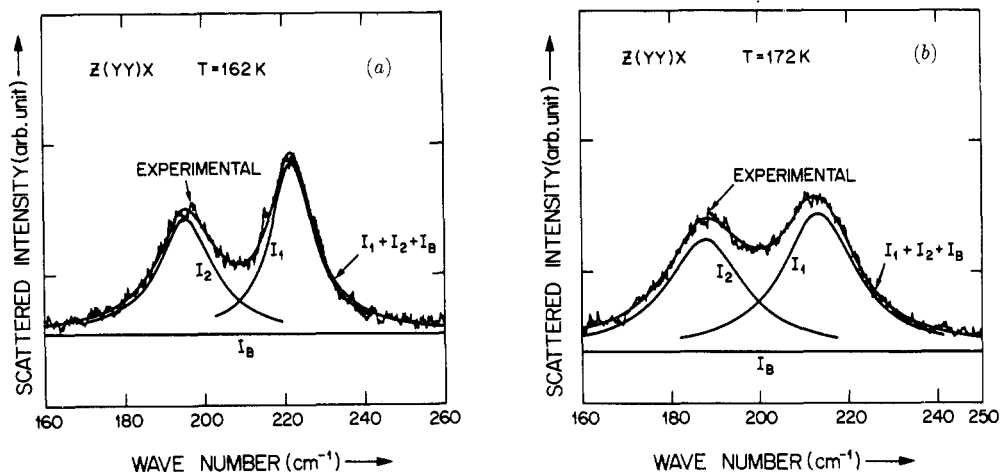
Figure 2. Curve fits of NH_4^+ translational Raman bands by the use of two Lorentzian components for: (a) ammonium sulphate, $\nu_1 = 222.0$ cm^{-1}, $\Gamma_1 = 7.4$ cm^{-1}, $S_1 = 8.0$, and $\nu_2 = 195.3$ cm^{-1}, $\Gamma_2 = 9.3$ cm^{-1}, $S_2 = 7.6$; (b) deuterated ($\sim$ 65%) ammonium sulphate, $\nu_1 = 213.0$ cm^{-1}, $\Gamma_1 = 10.9$ cm^{-1}, $S_1 = 9.8$, and $\nu_2 = 187.5$ cm^{-1}, $\Gamma_2 = 11.5$ cm^{-1}, $S_2 = 9.2$, single crystals in the ferroelectric phase. I_1 and I_2 are measured with respect to the background I_b.
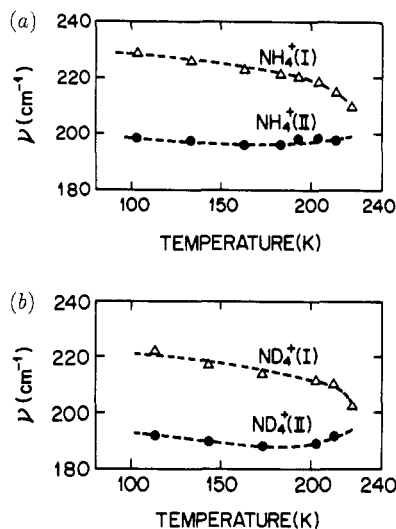

Figure 3. Temperature dependence of the frequencies of (a) the NH_4^+ translational bands and (b) the ND_4^+ translational bands as obtained from the curve fits. I_1 and I_2 are measured with respect to the background I_b.
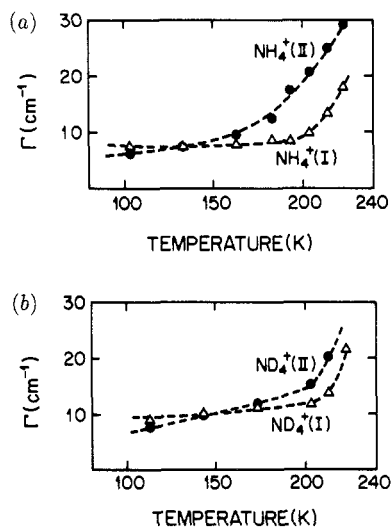
Figure 4. Temperature dependence of the bandwidth of (a) the NH_4^+ translational bands and (b) the ND_4^+ translational bands as obtained from the curve fits.

values of the observed Raman bands, $\nu_1/\nu_2 = 220.6/195.5 \simeq 1.128$. This translational mode is strongly coupled with the reorientational relaxation mode (Petzelt *et al* 1974).

In figures 3 and 4 the temperature dependences of the NH_4^+ translational bands (ν_1, ν_2 and Γ_1, Γ_2) are shown as obtained from the two-oscillator curve fitting of the observed Raman bands. The NH_4^+(II) band is seen hardly to change in frequency, but
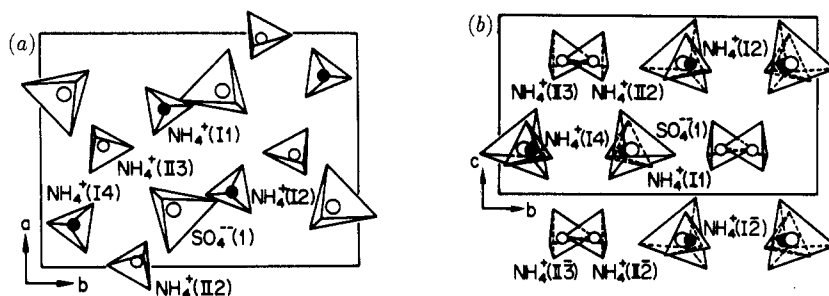
Figure 5. Schematic projections of the ammonium sulphate single crystal structure onto (*a*) the *ab* plane and (*b*) the *bc* plane at $T = 180$ K based on the neutron diffraction data (Schlemper and Hamilton 1966) of the atomic positions.

Table 1. Values of distances and direction cosine between SO_4^{2-} ion and NH_4^+ neighbour ions at $T = 180$ K in $(NH_4)_2SO_4$ calculated from the neutron diffraction data of Schlemper and Hamilton (1966).

NH_4^+ neighbours	Distance d (Å)	Direction cosine (α, β, γ)
$SO_4^{2-}(1)$–NH_4^+ (I4)	3.40	$(-0.14, -0.99, -0.01)$
$SO_4^{2-}(1)$–NH_4^+ (I1)	3.44	$(\ 1.00, -0.08, -0.01)$
$SO_4^{2-}(1)$–NH_4^+ (I2)	3.59	$(\ 0.17,\ 0.54,\ 0.82)$
$SO_4^{2-}(1)$–NH_4^+ (I4)	3.64	$(\ 0.16,\ 0.53, -0.83)$
$SO_4^{2-}(1)$–NH_4^+ (II2)	3.72	$(-0.47, -0.35,\ 0.81)$
$SO_4^{2-}(1)$–NH_4^+ (II2)	3.66	$(-0.48, -0.35, -0.80)$
$SO_4^{2-}(1)$–NH_4^+ (II3)	4.40	$(\ 0.50, -0.53,\ 0.69)$
$SO_4^{2-}(1)$–NH_4^+ (II3)	4.35	$(\ 0.50, -0.54, -0.68)$

to show a large decrease in bandwidth as temperature is lowered further below T_c until T $\simeq$ 100 K. The NH_4^+(I) band is seen to increase in frequency and decrease in bandwidth with decreasing temperature below T_c until above T $\simeq$ 190 K. Our results for the temperature dependence of the damping constant (Γ) seem to be consistent with the different orientational freezing temperatures of 90 K and 160 K for NH_4^+(II) and NH_4^+(I), respectively (Kydon *et al* 1967), and also with the different temperature dependences of the half width for the librational Raman bands of NH_4^+(II) and NH_4^+(I) (Iqbal and Christoe 1976). We can also see a stronger effect of deuteration on the NH_4^+(II) band, which may be indicative of the easier substitution at NH_4^+(II) sites, as is the case with alkali ionic substitution of NH_4^+ ions (Shiozaki *et al* 1977). If the Raman scattering strength S_1 and S_2 are assumed to be indicative of the degree of cooperative ordering of NH_4^+(I) and NH_4^+(II) ions, respectively, and thus directly related to the sublattice polarizations P_{1S} (> 0) and P_{2S} (< 0) of the ferri-electric structure (Sawada *et al* 1975), we may expect a higher temperature of zero polarization for the deuterated ammonium sulphate as observed by Unruh and Rüdiger (1972).

In order to accept and appreciate the important roles of NH_4^+(I) and NH_4^+(II) in the anomalous temperature dependence of the polarization, we may make a critical judgment against the point-charge model employing the permanent dipole moments of the distorted ions (Jain and Bist 1974). The point-charge model gives $P_s = 0.42$ μC cm^{-2}

Table 2. Point-charge model calculations of dipole moments p_a, p_b, p_c and polarization P_c associated with NH_4^+ (I), NH_4^+ (II), SO_4^{2-}, and the net polarization P_s in $(NH_4)_2SO_4$ based on the x-ray diffraction data of Hasebe (1981).

Temperature (K)	Ion(α)	$p_a(\alpha)$ (D)	$p_b(\alpha)$ (D)	$p_c(\alpha)$ (D)	$P_c(\alpha)$ (μC cm^{-2})
219.5	NH_4^+ (I)	−0.013	−0.140	−0.124	−0.334
	NH_4^+ (II)	0.062	−0.157	0.074	0.200
	SO_4^{2-}	−0.098	−0.025	−0.036	−0.096
					$P_s = -0.230$
209	NH_4^+ (I)	0.104	−0.096	−0.100	−0.269
	NH_4^+ (II)	−0.026	−0.175	0.124	0.334
	SO_4^{2-}	−0.113	−0.030	−0.009	−0.023
					$P_s = -0.042$
183	NH_4^+ (I)	0.008	−0.086	−0.227	−0.610
	NH_4^+ (II)	−0.009	0.028	−0.023	−0.061
	SO_4^{2-}	−0.123	−0.008	−0.020	−0.054
					$P_s = -0.725$
133	NH_4^+ (I)	−0.019	0.043	−0.130	−0.349
	NH_4^+ (II)	−0.131	0.172	0.067	0.180
	SO_4^{2-}	−0.127	−0.013	−0.029	−0.077
					$P_s = -0.246$

at 180 K (Jain and Bist 1974), in reasonable agreement with the experimental value of 0.34 μC cm^{-2} (Unruh 1970), when calculated on the basis of the neutron diffraction data of Schlemper and Hamilton (1966). We have applied the same point-charge model to obtain $P_s = 0.23$ μC cm^{-2} at 219.5 K, 0.04 μC cm^{-2} at 209 K, −0.73 μC cm^{-2} at 183 K and −0.25 μC cm^{-2} at 133 K when calculated on the basis of the x-ray diffraction data of Hasebe (1981) as shown in table 2. We can see that the results of the point-charge model calculations of the spontaneous polarization do not seem to be in agreement with the experimental observations, even in terms of the qualitative features of the temperature dependence, such as the positive maximum at just below $T_c = 223$ K and the gradual sign change from positive to negative (i.e polarization reversal) through zero polarization at around $T = 85$ K (Unruh 1970).

4. Conclusion

The point-charge model calculation of the spontaneous polarization in ammonium sulphate does not seem to explain the anomalous temperature dependence satisfactorily. Our results of Raman scattering studies of the NH_4^+ translational bands seem to support the two sublattice model of the non-equivalent NH_4^+(I) and NH_4^+(II) ionic groups (Sawada *et al* 1975), where the translational vibrations are strongly coupled with the reorientational relaxations (Petzelt *et al* 1974). The anomalous temperature dependence of the observed spontaneous polarization in ammonium sulphate may thus originate from the reorientational ordering of the NH_4^+(I) and NH_4^+(II) dipoles and also

the NH_4^+–SO_4^{2-} displacive lattice polarization, which was neglected in the point-charge model.

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