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Polarized Raman Spectra of $(NH_4)_2SO_4$ Single Crystals

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Synopsis. Polarized Raman spectra of $(NH_4)_2SO_4$ single crystals were measured at room temperature. The symmetry species of the observed Raman bands due to the internal vibrations of $SO_4{}^{2-}$ as well as the lattice modes were determined.

Several articles have appeared on the vibrational spectra of $(NH_4)_2SO_4$.[1–5] In spite of the importance of this crystals as one of the improper ferroelectrics, the vibrational problem does not seem to have been solved. The most thorough study is that by Torrie *et al.*[5] who measured infrared and Raman spectra of $(NH_4)_2SO_4$ and $(ND_4)_2SO_4$ powder at temperatures above and below the Curie point (−50 °C). Their results are convincing but do not determine the symmetry species of the infrared and Raman bands.

It is the purpose of this note to report the polarized Raman spectra of $(NH_4)_2SO_4$ single crystals in the paraelectric phase and to give the symmetry species of the Raman bands.

Experimental

Single crystals of $(NH_4)_2SO_4$ were grown from an aqueous solution by slow evaporation at room temperature. The crystals were obtained as thick plates (about 10 mm × 10 mm × 3 mm) with the broad face parallel to the (010) plane and the cleavage plane perpendicular to the *a*-axis. The crystal axes were checked by X-ray oscillation photographs. The polarized Raman spectra were recorded with a Shimadzu R-2D double monochrometer using photon counting detection. The 5145 Å line of an Ar^+ laser was used as the excitation wavelength with 700 mW power output. A polarization scrambler was placed between analyzer and slit and the wave numbers of the Raman bands were calibrated using spontaneous emission lines from the laser.

Results and Discussion

The crystal structure of $(NH_4)_2SO_4$ in the paraelectric phase is orthorhombic P_{nam}-D_{2h}^{16}, with four units of $(NH_4)_2SO_4$ in a Bravais unit cell.[6] All the ions occupy the sites with C_s symmetry.

Internal vibrations of the $NH_4{}^+$ ions are expected to appear between 3100 and 1400 cm^{-1}. However, because of their weak intensities in the Raman spectrum, polarization measurements were not successful. According to the factor group analysis, the Raman-active internal vibrations of the SO_4^{2-} ions are classified as $6A_g(\nu_1, \nu_2, 2\nu_3, 2\nu_4)+6B_{1g}(\nu_1, \nu_2, 2\nu_3, 2\nu_4)+3B_{2g}(\nu_2, \nu_3, \nu_4)+3B_{3g}(\nu_2, \nu_3, \nu_4)$ and the Raman-active lattice modes as $9A_g$(6 trans., 2 NH_4^+ lib., SO_4^{2-} lib.)$+9B_{1g}$(6 trans., 2NH_4^+ lib., SO_4^{2-} lib.) $+ 9B_{2g}$ (3 trans., 4 NH_4^+ lib., 2 SO_4^{2-} lib.)$+9B_{3g}$(3 trans., 4 NH_4^+ lib., 2 SO_4^{2-} lib.).

Polarized Raman spectra below 1200 cm^{-1} are shown in Fig. 1. The bands which appear between 1120 and 440 cm^{-1} are undoubtedly due to the internal modes (ν_1, ν_2, ν_3 and ν_4) of the SO_4^{2-} ions. In spite of the fact that ν_1 is inactive in B_{2g} and B_{3g} species, a very weak band is observed at 976 cm^{-1} in the spectra of both species. Imperfection in the crystal or the polarizer may be responsible for this. It should be noted that the relative intensity of the same vibrational mode belonging to A_g species can vary remarkably in the polarized spectra with different Raman tensor component. As can be seen in Fig. 1, the splitting of the internal modes of the SO_4^{2-} ions is not large. This is in accord with the result of the neutron diffraction study by Schlemper and Hamilton[6] that the SO_4^{2-} ions are not much distorted from tetrahedral symmetry.

The neutron inelastic scattering study at 172 K by Rush and Taylor[7] and the infrared study at 77 K by Torrie *et al.*[5] indicate that the librational modes of the NH_4^+ ions should appear around 330 cm^{-1}. In the present work, however, no band was observed between 440 and 200 cm^{-1}. This is probably because the $NH_4{}^+$ ions are almost in free rotation at room temperature.

The liberational modes of the SO_4^{2-} ions and the

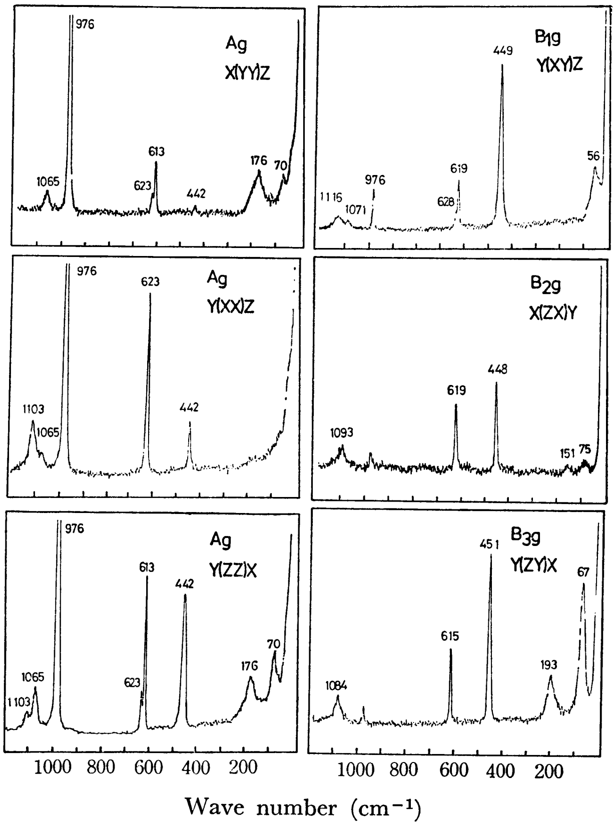

Fig. 1. Polarized Raman spectra of $(NH_4)_2SO_4$ single crystals. The Raman tensor components are expressed according to Porto's notation.[8]

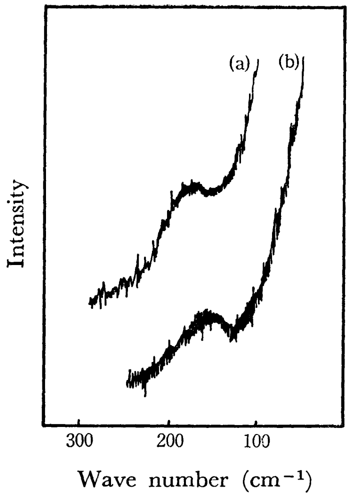

Fig. 2. Low frequency Raman spectra of (a) $(NH_4)_2SO_4$ and (b) $(ND_4)_2SO_4$ powder.

translational modes of the NH_4^+ and SO_4^{2-} ions are expected to appear below 200 cm^{-1}. The Raman spectra below 300 cm^{-1} of $(NH_4)_2SO_4$ and $(ND_4)_2SO_4$ powder are shown in Fig. 2. The band at 185 cm^{-1} of $(NH_4)_2SO_4$ shifts to 167 cm^{-1} by deuteration. The frequency ratio 185/167 is almost equal to $(22/18)^{1/2}$. This means that the band is attributed to the translational modes of the NH_4^+ ions. Thus, the bands at $176(A_g)$, $151(B_{2g})$ and $193(B_{3g})$ cm^{-1} in the polarized Raman spectra were assigned to the translational modes of the NH_4^+ ions.

Since the SO_4^{2-} ions do not differ significantly from the regular tetrahedral,[6] it is highly probable that the Raman intensity of the librational modes of the SO_4^{2-} ions is too weak to be detected. The bands at $70(A_g)$ $56(B_{1g})$, $75(B_{2g})$ and $67(B3_g)$ cm^{-1} in the polarized Raman spectra were therefore assigned to the translational modes of the SO_4^{2-} ions (Table 1).

Table 1. Observed Raman frequencies (cm^{-1}) and assignment of $(NH_4)_2SO_4$

Assignment		A_g	B_{1g}	B_{2g}	B_{3g}
Lattice modes					
SO_4^{2-} trans.		70	56	75	67
NH_4^+ trans.		176		151	193
Internal modes					
SO_4^{2-}	ν_2	442	449	448	451
	ν_4	613 623	619 628	619	615
	ν_1	976	976		
	ν_3	1065 1103	1071 1116	1093	1084

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