Temperature Dependence of the Lattice Vibrations of Triglycine Sulfate

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Far infrared spectra from 400 to 30 cm^{-1} of triglycine sulfate and its deuterated analogue were measured and the bands due to the librational modes of glycine molecules were identified. Polarized Raman spectra below 300 cm^{-1} of triglycine sulfate single crystals were measured and the symmetry species of the observed lattice vibrations were determined. Temperature dependence of the lattice vibrations was examined. Significant changes were detected in both infrared and Raman spectra on crossing the Curie temperature, indicating a flipping motion of glycine I in the paraelectric phase and suggesting the ferroelectric transition in triglycine sulfate to be of an order-disorder type.

Triglycine sulfate (TGS) is one of the few crystals which exhibit ferroelectricity at room temperature. Since its discovery in 1956 by Matthias *et al.*,[1] the crystal structure as well as ferroelectric transition have been extensively studied.

A detailed crystal structure was reported by Hoshino *et al.*[2] and recently by Itoh and Mitsui.[3] Hoshino *et al.* proposed an order-disorder type theory of the ferroelectric transition based on their X-ray diffraction data. They explained the dipole switching mechanism in the ferroelectric phase in terms of the flipping of the $\mathrm{NH_3^+CH_2COOH}$ glycinium ion (glycine I) between two equivalent orientations in the crystal, plus the tunneling of the hydrogen bonded proton between the $\mathrm{NH_3^+CH_2COO^-}$ zwitter-ion (glycine II) and the other $\mathrm{NH_3^+CH_2COOH}$ ion (glycine III).

The theory was supported by critical X-ray scattering study.[4] However, deuteron magnetic resonance studies[5,6] cast some doubt about the proposed dipole reversal mechanism and the order-disorder nature of the ferroelectric transition.

Infrared and Raman studies on TGS have been carried out by several investigators. Dodd[7] measured polarized infrared spectra from 4000 to 625 cm^{-1} and concluded that TGS, unlike crystalline glycine, was not in the zwitter-ion form. She further reported that heating the crystal above the Curie temperature (48 °C) produced no appreciable changes in the infrared spectra. Khanna *et al.*[8] investigated the infrared spectra of TGS and its deuterated analogue at room temperature and liquid $\mathrm{N_2}$ temperature and found the bands due to the zwitter-ion as well as glycinium ion. Recent investigation by Raman spectra[9] supported the presence of the zwitter-ion in TGS crystals.

Barker and Tinkham[10] measured polarized infrared reflection spectra down to 14 cm^{-1}, but no soft mode was observed. Sato[11] measured infrared spectra at various temperatures and found that the band at 575 cm^{-1} markedly decreased in intensity with temperature rise of the crystal, disappearing above the Curie temperature. Quilichini *et al.*[12] measured polarized Raman spectra below 200 cm^{-1} at various temperatures, but failed to reveal significant spectral changes due to ferroelectric transition.

The purpose of this paper is two-fold; to determine symmetry species of the lattice vibrations by polarized Raman spectra, and to detect changes in the infrared and Raman spectra by temperature variation and thereby giving additional information on the mechanism of the ferroelectric transition in TGS.

Experimental

Single crystals of TGS were grown from an aqueous solution containing glycine and sulfuric acid in proper molar proportions. The composition of the crystals were checked by titrating a small amount of the sample with a standard NaOH solution. The crystals were in the form of thick plates (about 7 mm × 7 mm × 3 mm) with a broad face parallel to the b-axis (two-fold axis) and a cleavage plane perpendicular to the b-axis.

The far infrared spectra (400—30 cm^{-1}) of TGS and its *N*-deuterated powder suspended in Nujol were recorded with a Hitachi FIS-3 spectrophotometer. The *N*-deuterated analogue was prepared by recrystallizing the sample several times from heavy water solutions.

The Raman spectra were recorded with a Shimadzu R-2D double monochrometer. The 5145 Å line of an $\mathrm{Ar^+}$ laser was used as the excitation wave-length with 700 mW power output. For the polarized Raman spectra, single crystals with three facets each respectively parallel to the cleavage plane (010), the optic plane $(\bar{1}02)$ and the plane perpendicular to both planes was used. The third facet was almost parallel to the (100) plane, the angle between them being less than 3°. A polarization scrambler, a quartz wedge, was placed between the analyser and slit to correct preferential sensitivity of the monochrometer to the polarization of the scattered light. The spectra were recorded by photon counting detection and the wave numbers of the Raman bands were calibrated using spontaneous emission lines from the laser.

The temperature variation of the infrared and Raman-spectra were measured using high and low temperature cells. For the infrared spectra a double chopping method was employed to eliminate the effect of the radiation from the sample and the reference. The temperature of the crystal was measured and controlled within ± 1°C by means of a copper-constantan thermocouple in the range -190 -25 °C and an alumel–chromel thermocouple in the range above 25 °C.

Results and Discussion

The crystal structure of TGS is monoclinic; the space group is C_2^2–$P2_1$ in the ferroelectric phase and C_{2h}^2–$P2_1/m$ in the paraelectric phase.[2,13] In either phase, the Bravais unit cell contains two units of the formula $\mathrm{NH_3^+CH_2COO^-(NH_3^+CH_2COOH)_2SO_4^{2-}}$. The crys-

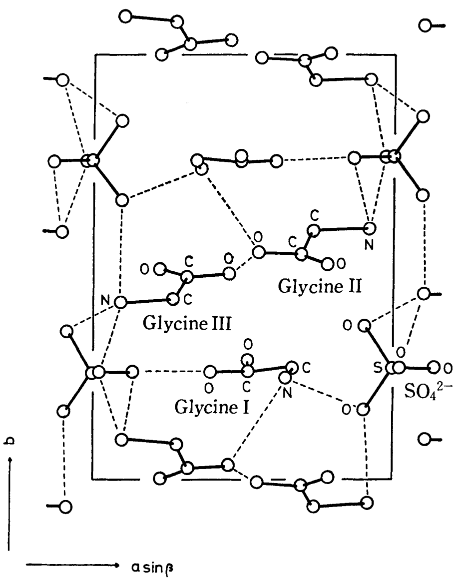

Fig. 1. Projection of the crystal structure of TGS on the ab-plane (ferroelectric phase). Positions of hydrogen atoms are not given. Hydrogen bonds are indicated by dotted lines.

tal structure in the ferroelectric phase is shown in Fig. 1. The lattice constants are: $a=9.417$, $b=12.643$, $c=5.735$ Å, and $\beta=110°23'$. The monoprotonated glycinium ions are denoted by glycine I and III, and the zwitter-ion by glycine II. The molecular plane of glycine I is tilted 12.5° with respect to the ac-plane. The transition from the ferroelectric to the paraelectric phase might be due to a statistical disorder in the orientation of the glycine I ions with respect to the ac-plane (y=1/4 and 3/4), *i.e.* above the Curie point, these planes become the mirror planes in a statistical sense.[3]

Assignment of Lattice Vibrations. The 45 optically active lattice modes can be classified by the usual group theoretical method as 23A+22B in the ferroelectric phase and $12A_g+12B_g+11A_u+10B_u$ in the paraelectric phase. Classification of the lattice vibrations is given in Table 1 together with the activities in the infrared and Raman spectra.

TABLE 1. CLASSIFICATION OF LATTICE VIBRATIONS OF TGS

(1) Ferroelectric Phase (C_2^2-$P2_1$)

	Trans	Lib.	IR	Raman
A	11	12(3)	M_z	α_{xx} α_{yy} α_{zz} α_{xy}
B	10	12(3)	M_x M_y	α_{xz} α_{yz}

(2) Paraelectric Phase (C_{2h}^2-$P2_1/m$)

	Trans	Lib.	IR	Raman
A_g	6	6(1)	ia	α_{xx} α_{yy} α_{zz} α_{xy}
B_g	6	6(2)	ia	α_{xz} α_{yz}
A_u	5	6(2)	M_z	ia
B_u	4	6(1)	M_x M_y	ia

Figures in parentheses donate the number of librational modes of SO_4^{2-}.

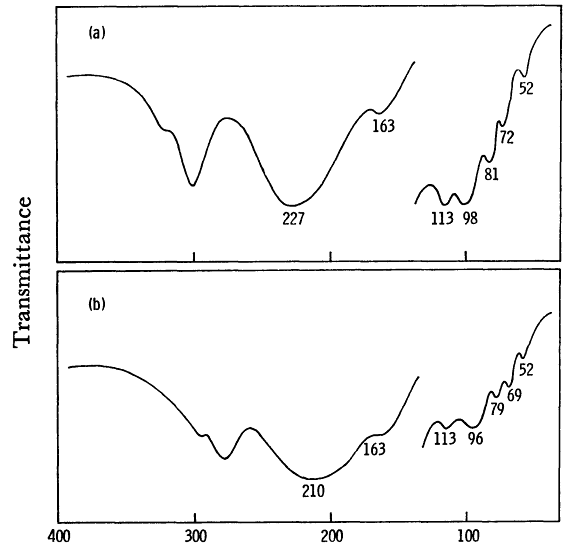

Fig. 2. Far infrared spectra of TGS and its deuterated powder suspended in Nujol.
(a) $NH_3^+CH_2COO^-(NH_3^+CH_2COOH)_2SO_4^{2-}$
(b) $ND_3^+CH_2COO^-(ND_3^+CH_2COOD)_2SO_4^{2-}$

The far infrared spectra from 400 to 30 cm⁻¹ of TGS and its deuterated analogue are given in Fig. 2. Lattice vibrations are observed at 52, 72, 81, 98, 113, 163, and 227 cm⁻¹. The bands at 72, 81, 98, and 227 cm⁻¹ shift respectively to 69, 79, 96, and 210 cm⁻¹ by deuteration of the NH_3^+ group, while those at 52, 113, and 163 cm⁻¹ remain unchanged. Accordingly, the bands at 72, 81, and 98 cm⁻¹ can be assigned to the librational modes of the glycine molecules, and the band at 227 cm⁻¹ being atrributable to the lattice mode associated with hydrogen bonds. The shift of the band at 227 cm⁻¹ is slightly greater than that expected from the change of the moment of inertia. However, this band is undoubtedly overlapped by more than one band and its peak shift can not be determined accurately. The bands at 52, 113, and 163 cm⁻¹ could be assigned either to librational modes of SO_4^{2-} or to translational modes.

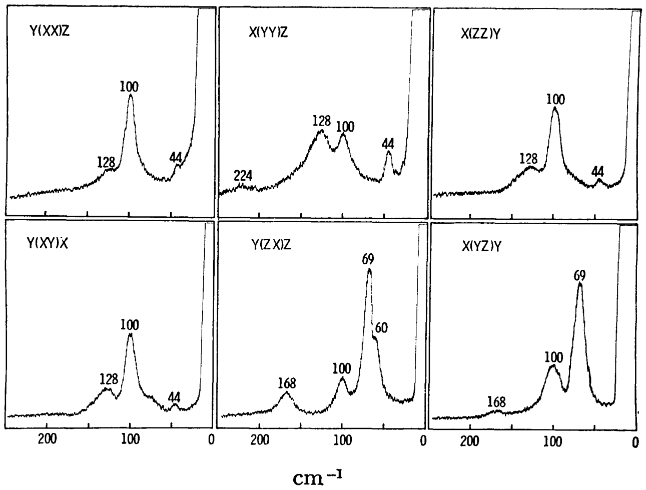

Fig. 3. Polarized Raman spectra of TGS single crystals. The Raman tensor components are expressed according to Porto's notation.

The polarized Raman spectra of TGS single crystals are shown in Fig. 3. The Raman tensor components are expressed in terms of the notation of Damen *et al.*[14] The lattice vibrations are detected at 44, 60, 69, 100, 128, 168, and 224 cm^{-1}. The frequencies agree with the values in literatures.[15–17] We see from Fig. 3 that the bands at 44, 128, and 224 cm^{-1} belong to symmetry species A and those at 60, 69, and 168 cm^{-1} to species B. The band at 100 cm^{-1} is overlapped by lattice modes belonging to species A and B. In the spectrum at liquid N_2 temperature, the band splits into three bands at 93, 101, and 111 cm^{-1}.

TABLE 2. FREQUENCIES (cm^{-1}) OF LATTICE VIBRATIONS OF TGS AND ASSIGNMENTS

IR (powder)	Raman (single crystal)	Symmetry species	Assignment
	44	A	
52			
	60	B	
72	69	B	Lib. (glycine)
81			Lib. (glycine)
98	100	A+B	Lib. (glycine)
113			
	128	A	
163	168	B	
227	224	A	H-bonds[a]

a) A lattice mode associated with hydrogen bonds.

The frequencies of the lattice modes observed in the infrared and Raman spectra are summarized in Table 2 along with some of their general assignments. The Raman spectra of TGS crystals cut at 45° to the b-axis were also measured in order to identify the longitudinal modes. However, no TO–LO splitting was observed.

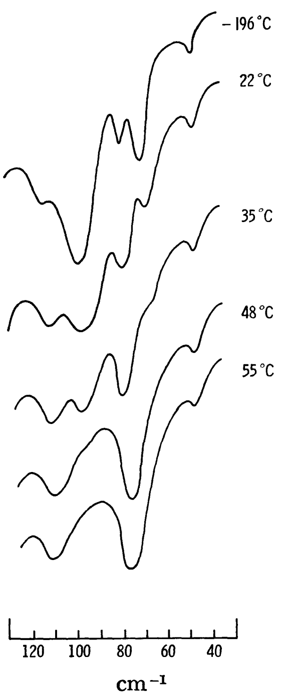

Fig. 4. Temperature dependence of the infrared bands of TGS powder.

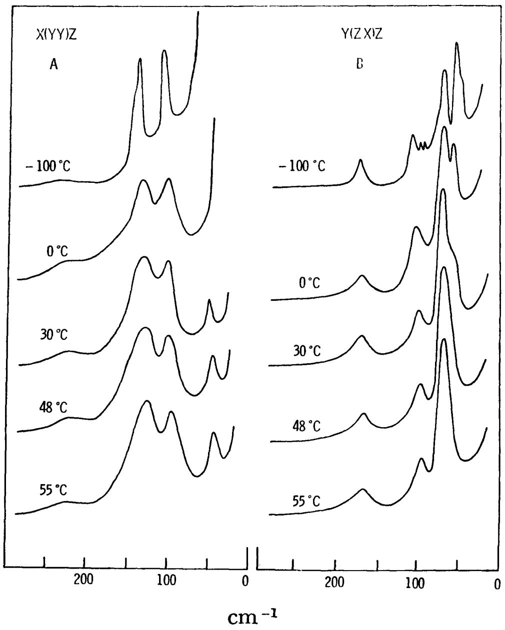

Fig. 5. Temperature dependence of the Raman bands of TGS single crystals.

Temperature Variation. The far infrared spectra from 130 to 30 cm^{-1} at liquid N_2 temperature and elevated temperatures are shown in Fig. 4. The band at 98 cm^{-1} gradually decreases in intensity with the rise in temperature of the crystal disappearing completely in the paraelectric phase (above 48 °C). The band at 72 cm^{-1} also seems to disappear above the Curie temperature, although it is probably masked by the near-by band at 81 cm^{-1} which gradually shifts to lower frequencies and become more intense and broad with the rise in temperature. The polarized Raman spectra below 250 cm^{-1} at various temperatures are reproduced in Fig. 5. It is seen that the band at 60 cm^{-1} which belongs to B symmetry species gradually decreases in intensity as the temperature rises and fades away above the Curie temperature.

As the crystal changes from non-centrosymmetric structure C_2^2 to centrosymmetric structure C_{2h}^2 at the Curie point when the crystal is heated, it is possible that the disappearance of the infrared and Raman bands is caused by the difference in the selection rule. If this is the case, the lattice vibration corresponding to the infrared band at 98 cm^{-1} should become a "gerade" mode in the paraelectric phase, intensity enhancement of the Raman band arising from this lattice mode thus being expected. Further, the lattice vibration corresponding to the Raman band at 60 cm^{-1} should be an "ungerade" mode in the paraelectric phase, giving rise to a strong band in the infrared spectrum. However, the Raman band at 100 cm^{-1} does not seem to exhibit appreciable intensity changes by temperature variation, and the band corresponding to the Raman band at 60 cm^{-1} can not be detected in the infrared spectrum.

The disappearance of the infrared band at 98 cm^{-1} and the Raman band at 60 cm^{-1} can be explained satisfactorily if we assume that these bands arise from

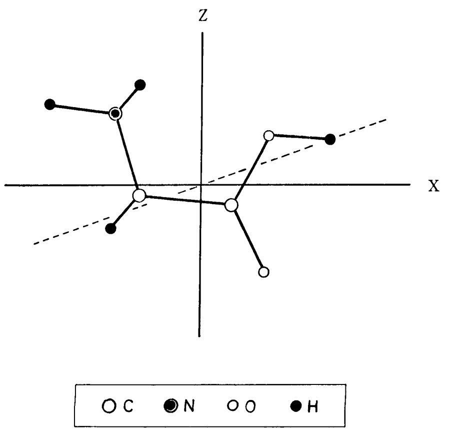

Fig. 6. Principal axes of the monoprotonated glycinium ion. The direction of the dipole moment is also shown by a dotted line.

the librational mode around the z axis of glycine I (Fig. 6). According to the crystal structure proposed by Hoshino *et al.*,[2)] the molecular plane of glycine I makes an angle of 12.5° with the ac-plane in the ferroelectric phase, while in the paraelectric phase, glycine I performs a flipping motion between the two equivalent tilted positions with respect to the ac-plane. Because of this flipping motion, the infrared and Raman bands due to the librational modes of glycine I ions around the z axis might be smeared over the spectrum and their peaks would not be detected above the Curie temperature (48 °C). We see from Figs. 4 and 5 that the intensity decrease of the bands at 98 and 60 cm^{-1} starts at a temperature much lower than the Curie point. This is probably because the flipping motion of glycine I in the ferroelectric phase does not abruptly 'freeze in' at the Curie point but persists to some extent in the ferroelectric phase.

It is interesting to see that the intensity of the infrared band at 81 cm^{-1} gradually increases as the temperature of the crystal increases. The band can be assigned to the librational mode in which glycines II and III librate out-of-phase. In the paraelectric phase, TGS crystals have a center of symmetry between glycines II and III and hence glycines II and III must be in the same configuration, implying that one proton tunnels between them. Thus, the dipole moment of these two molecules in the paraelectric phase might differ from that in the ferroelectric phase and the intensity enhancement of the infrared band at 81 cm^{-1} is attributable to the change in the dipole moment.

Savatinova and Simova[18)] carried out temperature variation of the low frequency Raman spectra of TGS powder using a mercury lamp as the exciting source and concluded that the frequency of the band at 70 cm^{-1} decreases to zero near the temperature of the phase transition. However, their conclusion is inconclusive since this band is heavily overlapped by the band at 60 cm^{-1} and moreover, these two bands are masked by the exciting line of the mercury lamp and the behavior of the band in their experiment is not clear in detail. We see in Fig. 5 that the band at 69 cm^{-1} in fact shifts somewhat to lower frequencies as the temperature rises. However, the frequency of this band does not go to zero even in the paraelectric phase.

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