

## Nature of the Ferroelectric Transition in Triglycine Sulfate

R. BLINC, S. DETONI, AND M. PINTAR

*J. Stefan Nuclear Institute, Ljubljana, Yugoslavia and Ljubljana University, Ljubljana, Yugoslavia*

(Received September 2, 1960)

The occurrence of linewidth transitions in the proton magnetic resonance spectra of triglycine sulfate, selenate, and fluoberyllate at the corresponding Curie points demonstrates that the ferroelectric transitions in these crystals are connected with a rearrangement of the basic ionic units in the unit cell. The results of a combined proton magnetic and infrared study confirm the crystal structure proposed by Pepinsky and co-workers. Further they show that the ferroelectric transition in triglycine sulfate and its isomorphs is of the order-disorder type and basically of the same nature as that in  $\text{KH}_2\text{PO}_4$ . The chief difference is the strong coupling of the protonic motion in triglycine sulfate with the motions of heavier groups.

IN the last few years ferroelectric transitions have been discovered in a considerable number of hydrogen-bonded crystals. Although these crystals possess certain structural features common to all of them, no comprehensive theory of the ferroelectric transitions exists as yet. A number of mechanisms have been proposed, which sometimes contradict one another. A definite choice between them should be possible only with a detailed knowledge of the nature of the transitions in a series of these crystals.

The object of this paper is to find out whether the ferroelectric transitions in  $(\text{glycine})_3\text{H}_2\text{SO}_4$  and its isomorphs, a relatively new group of ferroelectric materials, can be explained, in principle, by the same mechanism as those in  $\text{KH}_2\text{PO}_4$  and  $\text{KH}_2\text{AsO}_4$ .

The dielectric and thermal properties<sup>1</sup> of triglycine sulfate (TGS), triglycine selenate (TGSe), and triglycine fluoberyllate (TGBe) have been studied in detail and the ferroelectric transitions found to be of second order. The transition temperatures are 47°C, 22°C, and 70°C for TGS, TGSe, and TGBe, respectively.<sup>1</sup> The crystal structure of TGS in the ferroelectric phase has been studied by Hoshino, Okaya, and Pepinsky and the coordinates of all except hydrogen atoms have been determined.<sup>2</sup> The positions of the hydrogen atoms have been assumed tentatively and a dipole reversal mechanism was proposed, based on the existence of a short hydrogen bond ( $R_{\text{O}\cdots\text{O}} = 2.43 \text{ \AA}$ ) with a noncentral hydrogen. The nonferroelectric phase should be disordered, while in the ferroelectric phase the proton should occupy a position closer to  $\text{O}_{\text{III}}$  than to  $\text{O}_{\text{II}}$ , following the nomenclature of Pepinsky. A neutron diffraction study which has been claimed to confirm the assumed asymmetry in the hydrogen position is not yet completed and so the nature of the transition is not fully clear.

It occurred to us that the present knowledge of the crystal structure makes it worthwhile to undertake a combined proton magnetic resonance and infrared study. It was hoped to get independent evidence of the proposed dipole reversal mechanism as well as additional information on the nature of the transition.

The temperature dependence of the second moments of the proton magnetic resonance absorption lines of polycrystalline TGS, TGSe, and TGBe is given in Fig. 1. All the substances investigated exhibit two linewidth transitions, a low-temperature one with the center at  $-120^\circ\text{C}$  approximately, and a second one with the center at the corresponding Curie point. An approximate calculation of the "rigid lattice" second moment for TGS, by assuming a 1.015- $\text{\AA}$  N—H bond

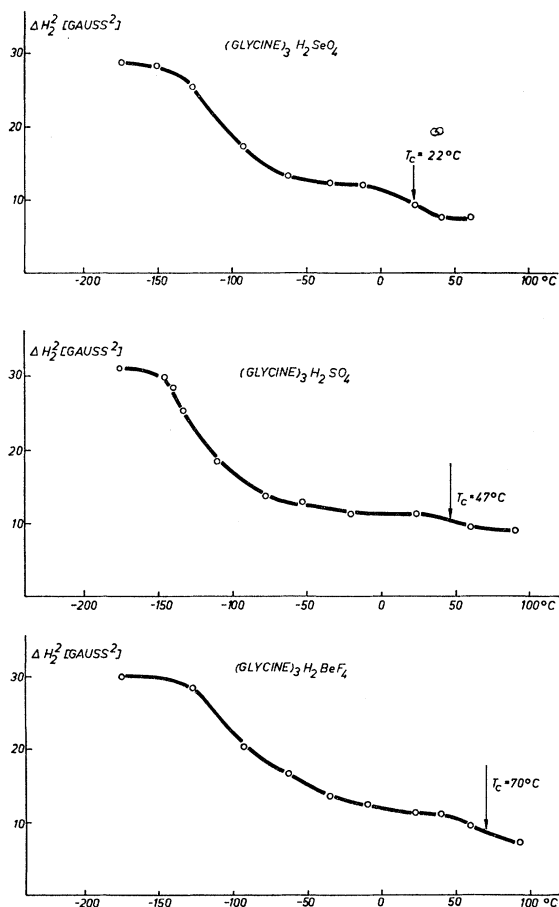


FIG. 1. Second moment of the proton magnetic resonance absorption in polycrystalline triglycine sulfate, selenate, and fluoberyllate plotted against temperature.

<sup>1</sup> S. Hoshino, T. Mitsui, F. Jona, and R. Pepinsky, Phys. Rev. **107**, 1255 (1957).

<sup>2</sup> S. Hoshino, Y. Okaya, and R. Pepinsky, Phys. Rev. **115**, 323 (1959).

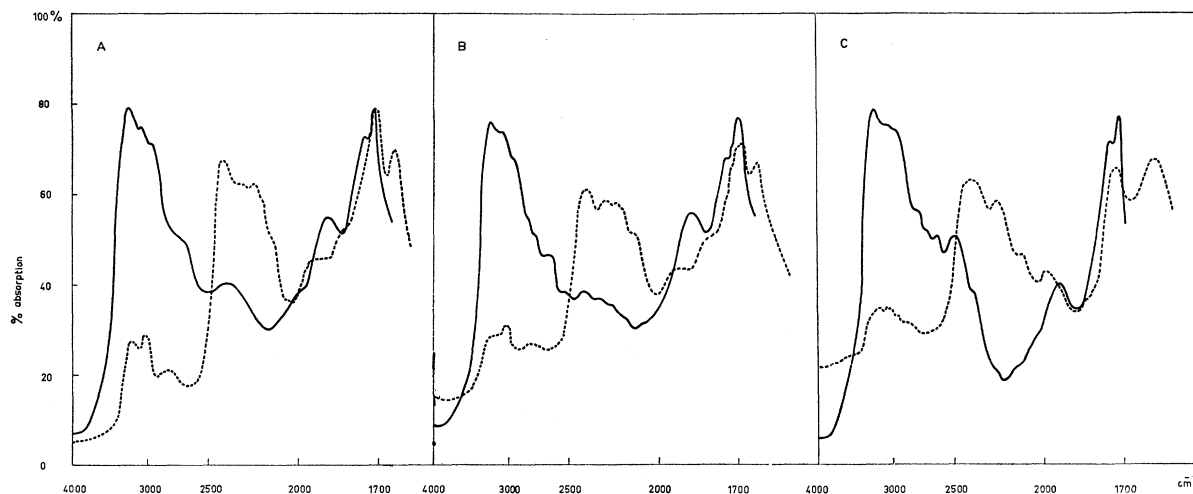


Fig. 2. Infrared spectra of (A) TG sulfate (full line: undeuterated; dashed: partially deuterated); (B) TG selenate (full line: undeuterated; dashed: partially deuterated); (C) TG beryllate (full line: undeuterated; dashed: partially deuterated).

length and the structure proposed by Hoshino *et al.*, is in reasonable agreement with the experimental data below the low-temperature transition, thus confirming the proposed crystal structure. The magnitude of the change of the second moment at  $-120^{\circ}\text{C}$  shows that this transition is due to the onset of reorientation of the  $\text{NH}_3^+$  groups about the  $C_3$  axis at a rate higher than  $10^4$  cps.

The existence of a second linewidth transition in the spectrum of polycrystalline TGS (Fig. 1) is confirmed by a single crystal proton magnetic resonance study. This revealed marked changes in the line shapes and second moments ( $3G^2$ ) in some orientations above and below the Curie point. The magnitude of the changes shows that, in addition to the OH protons, glycine ions as a whole are involved in the transition.

The occurrence of a transition in all three isomorphous crystals at the corresponding Curie points demonstrates that the ferroelectric process in this group of crystals is connected with a rearrangement of the protons sites and so confirms the basic assumption of Pepinsky *et al.*

The above data, however, cannot by themselves distinguish between two possible interpretations of the nature of the ferroelectric transition. According to the first, the transition is of the static displacive type. At the Curie point, the protons in single minimum hydrogen bonds displace from symmetric or statistically symmetric positions to asymmetric ones, triggering the rearrangement of the glycine ions. According to the second, the rearrangement of the proton sites at  $T_C$  may be explained in terms of a dynamic model involving a change from a symmetric double potential well for the protons into an asymmetric one below  $T_C$ . This model implies a dynamic order-disorder transition of the basic ionic units in the unit cell with a fair amount of disorder below  $T_C$ .

In order to clarify this point, the infrared spectra of

TGS, TGSe, and TGBe and their deuterated analogs have been recorded. The spectra were studied both above and below the Curie points, as well as at liquid nitrogen temperature.

Two types of hydrogen bonds with O—O distances of 2.43 and 2.54 Å exist in TGS, and the OH stretching bands are accordingly expected to occur in the region between 2700 and 1700  $\text{cm}^{-1}$ . Indeed, bands were found at 2680, 2360, and 1870  $\text{cm}^{-1}$ , thus again supporting the proposed crystal structure. The change of frequency of these bands upon deuteration together with their non-appearance in the Raman spectrum,<sup>3</sup> proves that these bands are due to vibrations involving protons of the O—H groups. Their polarization properties<sup>4</sup> and their appearance at nearly the same place in all three isomorphous crystals (Fig. 2) strongly suggest that they are fundamental bands and not combinations. In particular, difference tones may be excluded because cooling does not reduce the relative intensity of any of these bands. Thus the 2680- $\text{cm}^{-1}$  band may be tentatively assigned as the OH stretching band of the longer hydrogen bond, and the 2360 and 1870- $\text{cm}^{-1}$  bands as belonging to the shorter H bond, which should be the main reversible dipole in crystal.

TABLE I. OH and OD absorption frequencies in the region between 2700 and 1700  $\text{cm}^{-1}$  for triglycine sulfate, selenate, and fluoberyllate.

TGS		TGSe		TGBe	
OH	OD	OH	OD	OH	OD
2680	1920	2680	1910	2710	1990
2360	1820	2400	1810	2380	1820
1870		1860		1930	

<sup>3</sup> R. S. Krishnan and K. Balasubramanian, Proc. Indian Acad. Sci. A48, 138 (1959).

<sup>4</sup> D. M. Dodd, Spectrochim. Acta 15, 1072 (1959).

The static explanation of the ferroelectric transition implies at  $T_c$  a fair amount of shortening (up to 0.1 Å) of the (OH) bond, which belongs to the shorter hydrogen bridge. According to the bond length vibration frequency relation of Badger<sup>5</sup> this should result in a marked increase of the OH stretching frequency. No such changes have, in fact, been observed, and so the static model may be rejected.

On the other hand, the observed data are entirely consistent with the dynamic model, which implies no significant changes in the bond distances. The changes in the  $\nu_{OH}$  bands on going from the nonsymmetrical double minimum to the symmetrical double minimum potential field should be small and, in view of the broadness of the OH bands, hardly recognizable.

From the above data further informations on the shape of the potential field may be derived. The two bands at 2360 and 1870  $\text{cm}^{-1}$  could be, as in the case of  $\text{KH}_2\text{PO}_4$ ,<sup>6</sup> explained as  $\nu_{0+} \rightarrow \nu_{1-}$  and  $\nu_{0-} \rightarrow \nu_{1+}$  transitions. The apparent doubling of the OH stretching bands would thus be a consequence of a large splitting of the protonic vibrational levels due to the tunnel effect.

However, since these two bands are polarized in different directions and the 1870- $\text{cm}^{-1}$  band becomes considerably sharper on cooling, we have to modify the above explanation. The 2360- $\text{cm}^{-1}$  band is assigned as the OH stretching and the 1870  $\text{cm}^{-1}$  as most probably being the OH deformation frequency. The appearance of only one OH stretching band demonstrates that the splitting of the vibrational levels is so small, that the  $\nu_{0+} \rightarrow \nu_{1-}$  and  $\nu_{0-} \rightarrow \nu_{1+}$  transitions are not resolved. This requires a fairly high intervening potential barrier, which can result in view of the shortness of the O—O distance only from strong coupling of the protonic motions with the motions of heavier groups.

The above explanation is consistent with the proton magnetic resonance spectra. The existence of a line-width transition at the Curie point means, that accord-

ing to the dynamical model the proton reorientation frequency in the short hydrogen bond is so low that the increase in the hindering potential at the onset of long range order reduces its value below  $10^4$  cps. The reorientation frequency is thus much lower than that in  $\text{KH}_2\text{PO}_4$ , where the O—O distance is not so short. This can be explained only as a consequence of coupling of the protonic motions in TGS with the motions of heavier groups, which is absent in  $\text{KH}_2\text{PO}_4$ .

Another argument in favor of the proposed model is offered by the raise of the Curie point of TGS on deuteration.<sup>7</sup> This isotope effect may be explained in the same way as in  $\text{KH}_2\text{PO}_4$ , namely as resulting from an increased effective dipole moment in the deuterated crystal<sup>8</sup> due to the change in the vibrational energy levels.

In conclusion, we see that the present results confirm the crystal structure, proposed by Hoshino *et al.* Furthermore, they show that the ferroelectric transition is connected with an order-disorder rearrangement of the basic ionic units in the unit cell, and may be understood in terms of a dynamic model involving a change from a symmetric double minimum to an asymmetric double minimum potential well for the protons in the short hydrogen bonds. The nature of the ferroelectric transition in TGS and its isomorphs is thus, in principle, the same as in  $\text{KH}_2\text{PO}_4$ , the chief difference being the strong coupling of the protonic motions in TGS to the motion of heavier groups.

#### ACKNOWLEDGMENTS

The authors wish to thank Dr. R. Nitsche of the RCA Laboratories, Zürich, for supplying the TG sulfate, selenate, and fluoberyllate single crystals, I. Zupančič, who built the NMR spectrometer, M. Schara for the preparation of the samples, Professor D. Hadži for stimulating discussions, and Professor I. Kuščer for reading the manuscript.

<sup>5</sup> R. M. Badger, J. Chem. Phys. 2, 128 (1934).

<sup>6</sup> R. Blinc and D. Hadži, Molecular Phys. 1, 391 (1958).

<sup>7</sup> B. T. Matthias *et al.*, Bell Labs. Record 35, 271 (1957).

<sup>8</sup> R. Blinc, J. Phys. Chem. Solids 13, 204 (1960).