

A low-temperature phase transition in ferroelectric triglycine sulphate

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 L249

(<http://iopscience.iop.org/0953-8984/4/15/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 11:45

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

A low-temperature phase transition in ferroelectric triglycine sulphate

F Y El-Eithan, A R Bates, W Gough and D J Somerford

Department of Physics and Astronomy, University of Wales College of Cardiff, PO Box 913, Cardiff CF1 3TH, UK

Received 19 February 1992

Abstract. Results of a low-temperature Raman and ultrasonic investigation of triglycine sulphate (TGS) and its deuterated isomorph (DTGS) are presented. The existence of low-temperature phase transitions at 110 K and 130 K in TGS and DTGS respectively is considered. A large isotopic shift indicates that the transitions involve ordering of the NH_3 (ND_3) groups.

Triglycine sulphate (TGS), chemical formula $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$, has been extensively studied and exploited particularly with respect to its ferroelectric phase transition at $T_c = 49^\circ\text{C}$. In the paraelectric phase TGS is monoclinic with the centrosymmetric space group $P2_1/m$; below T_c the mirror plane disappears and the space group is $P2_1$. There are two formula units per unit cell. Each formula unit contains three different glycine ions GI, GII and GIII. GI ($\text{NH}_3^+\text{CH}_2\text{COOH}$) is non-planar, but GII ($\text{NH}_3^+\text{CH}_2\text{COOH}$) and GIII ($\text{NH}_3^+\text{CH}_2\text{COO}^-$) are planar and have a pseudo-centre of symmetry. Above T_c , the majority opinion is that GI is switching rapidly between two equilibrium positions, but in the hydrogen-bonded ferroelectric phase it occupies one of its preferred sites producing a dipole moment parallel to the b -axis. In the ferroelectric phase, the pseudo-centre of symmetry disappears and GII and GIII occupy non-equivalent sites.

The NH_3 groups attached to GI, GII and GIII are rapidly rotating about their C_3 axes both above and below T_c . Nuclear spin relaxation studies for the paraelectric phase (Blinic *et al* 1966) have shown the existence of both a 'slow' reorientation process associated with the strongly bonded $\text{NH}_3(\text{II})$ and $\text{NH}_3(\text{III})$ groups and a 'fast' reorientation process associated with $\text{NH}_3(\text{I})$. Proton magnetic resonance studies (Blinic *et al* 1961) have shown a linewidth anomaly at around 150 K thought to be associated with the slow process.

The purpose of this letter is to present new results of a Raman and ultrasonic investigation of TGS and its deuterated isomorph DTGS. The object of our study was to try to obtain information on the NH_3 -group reorientation process in the crystal. Our results, discussed below, indicate a new low-temperature phase transition. The Raman experiments were carried out in right-angled geometry using 514.5 nm radiation. The scattered radiation was analysed using a Coderg T800 spectrometer, and signal processing was carried out using a Digital Minc 11 microcomputer. The sample was maintained in a Thor Cryogenics cryostat at accurately controlled temperatures (± 0.01 K). Crystal axes were labelled according to Konstantinova *et al* (1959).

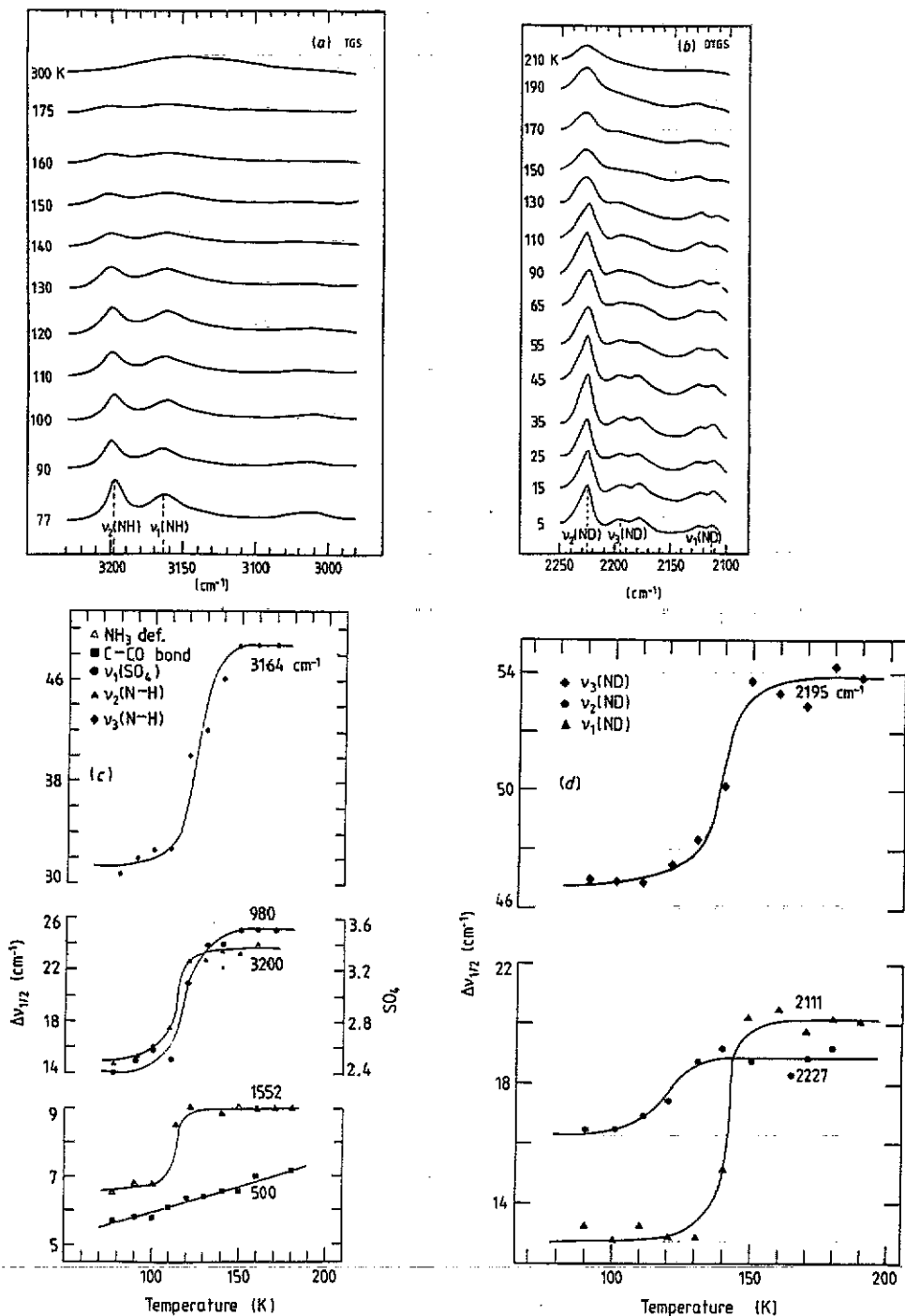


Figure 1. (a) Behaviour of the stretching vibrations of NH_3 in TGS through the low-temperature phase transition. (b) Behaviour of the stretching vibrations of ND_3 in DTGS through the low-temperature phase transition. (c) Temperature dependence of the linewidth of the N-H stretching, NH_3 deformation, C-CO bond and SO_4 vibrations in TGS. (d) Temperature dependence of the linewidth of the N-D stretching vibrations in DTGS.

For the ultrasonic part of this investigation, suitable samples were cut and polished and crystallographic directions were checked using the back-reflection Laue technique. The two-way transit times of short 30 MHz pulses propagating along the principal directions were determined. Difficulties associated with the conventional Nonaq bonding material below 150 K were probably due to the relatively large differential thermal expansivity at the quartz and TGS interface. Below 150 K and down to 80 K a methylcyclohexane bond was used (Rehwald 1980). The samples were cooled in a conventional continuous-flow cryostat (Thor Cryogenics). A cooling rate of 0.1 K min^{-1} was maintained through the phase transition, allowing simultaneous measurement of ultrasonic velocity and attenuation.

The Raman spectrum of TGS has been the subject of several studies, notably by Cervenka *et al* (1975) and Winterfeldt *et al* (1977). The latter includes the only previous low-temperature work, with spectra at fixed low temperatures. The NH_3 valence vibrations were not seen. Figures 1(a) and 1(b) show the N-H stretching region for TGS and DTGS in which the NH_3 valence vibrations are resolved. Figures 1(c) and 1(d) show the temperature dependencies of some internal-mode halfwidths. $\nu_1(\text{NH})$, $\nu_2(\text{NH})$ and $\nu_1(\text{SO}_4)$ show sudden changes near 110 K in the case of TGS and near 130 K in DTGS. Internal modes associated with skeletal vibrations of glycine molecules show no anomalous behaviour (e.g. the C-CO bond for TGS, figure 1(c)).

Figures 2 and 3 show the temperature variation of the sound velocity and the attenuation along (100), (010) and (001) for TGS and DTGS respectively. TGS shows attenuation and slight mode softening near 108 K, and DTGS shows similar behaviour near 134 K. The velocity change amounts to about 0.1%.

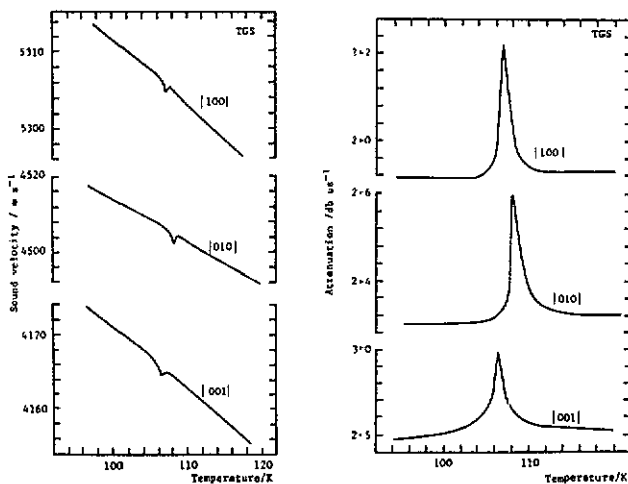


Figure 2. Temperature variation of velocity and attenuation of longitudinal sound waves in TGS.

We believe that these results point to the existence of low-temperature phase transitions in these crystals; the large isotopic shift indicates that the transitions involve ordering of the NH_3 (ND_3) groups. This interpretation is consistent with changes in NH_3 linewidths, and, because the SO_4 groups are also bonded to the NH_3 groups, an anomaly in the linewidths of these internal modes would also be expected.

Figures 4 and 5 show the low-frequency spectra of TGS and DTGS for $x(yy)z$ and $z(xx)y$ geometry respectively. The spectra show little change through both transition

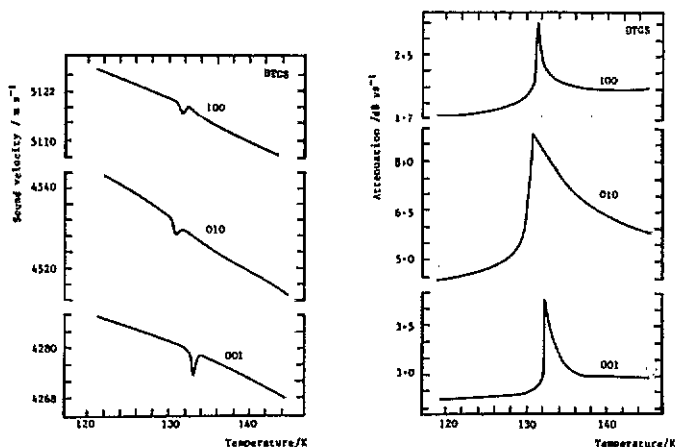


Figure 3. Temperature variation of velocity and attenuation of longitudinal sound waves in DTGS.

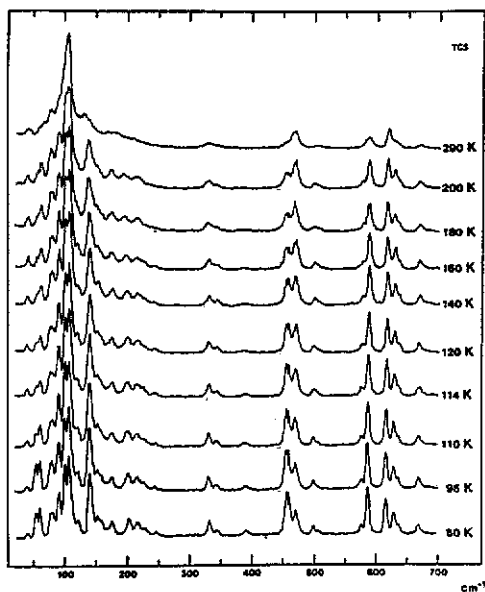


Figure 4. Spectra for TGS in the $x(yz)z$ geometry.

regions, but in both isomorphs the 57 cm^{-1} modes split and start to grow in intensity in the vicinity of the suggested transition temperatures. This mode has been previously assigned to a lattice vibration of the GI molecules; it appears therefore that the phase transition involves some structural reorganization of the heavy molecules in addition to ordering of the NH_3 (ND_3) groups.

The Raman and NMR experiments probe essentially different aspects of reorientation in solids; typical correlation times in the Raman experiments are $1 \times 10^{-12}\text{ s}$, whereas they are $1 \times 10^{-6}\text{ s}$ in NMR experiments. The proton magnetic resonance experiments of Blinc *et al* (1961) indicate a change in the second moment as the temperature is raised through 150 K which is interpreted as the onset of reorientation of NH_3^+ groups about the C_3 axis at a rate higher than 10^4 Hz . Temperature-dependent

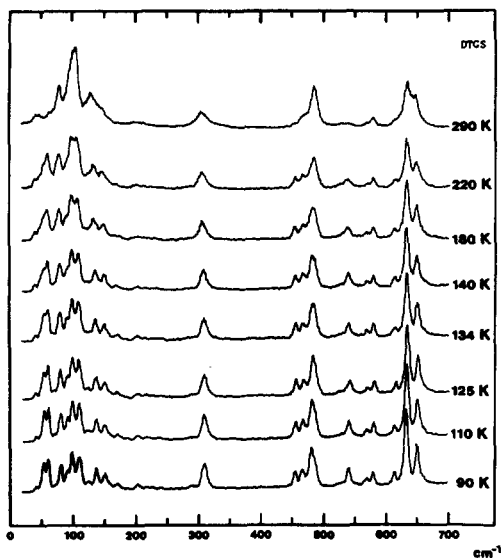


Figure 5. Spectra for DTGS in the $z(xx)y$ geometry.

studies of deuteron NMR spectra in DTG by Hoffman and Szczepaniak (1979) show that below about 200 K the spectrum is complicated by the slowing-down of ND_3 -group reorientations. The ND_3 group belonging to GI is found to rotate faster than those belonging to GII and GIII, and the results are consistent with the nuclear spin relaxation studies of Blinc. Several pieces of evidence, therefore, point to slowing down of NH_3 (or ND_3) reorientations with decreasing temperature and indicate that near 150 K the reorientation rates are about 10^4 – 10^5 Hz. The Raman linewidths behaviour, as shown in figure 1, has a temperature dependence characteristic of a thermally activated reorientation. Reorientation rates of the same order as those suggested by the resonance experiments would not affect the Raman spectrum; a thermally activated reorientation model gives a correlation time of about 3×10^{-12} s.

There are two main possibilities as explanations of the low-temperature phase transition. First, the phase transition is caused by the dynamics of at least one of the NH_3 (ND_3) groups. The shape of the Raman linewidth versus temperature curve should reflect site occupancy in some way. The fact that the GI lattice frequency is split would then indicate that the NH_3 (I) group is the driving group. The NMR experimental observations would then need to be related to simultaneous reorientations of two or more HN_3 groups or, more probably reorientation of the groups about axes other than their principal C_3 axes.

The second possibility is that the phase transition is unrelated to NH_3 reorientation in anything but a superficial way, but that the crystal behaves rather like Rochelle salt and becomes paraelectric again below 108 K and 134 K respectively. The lack of the dipole movement in the ferroelectric phase is provided by the NH_3 (I) molecule, and any rearrangement of this group would affect the Raman linewidth in a discontinuous way and would be likely to cause changes in the low-frequency spectrum. Such a possibility was proposed by Ganesan (1962) in his thermal expansion work. Support for this latter interpretation has been obtained recently in our laboratories from bulk measurements of dielectric properties (Al-Allack, private communication).

If the latter interpretation is correct, the large isotopic shift in the transition temperature is an indication of the importance of the part played by the NH_3 (ND_3) group.

References

- Blinic R, Detoni S and Pintar M 1961 *Phys. Rev.* **124** 1036-8
Blinic R, Lahajnar, Pintar M and Zupancic I 1966 *J. Chem. Phys.* **44** 1784-7
Cervenka S O, Prasad Rao A D and Porto S P S 1975 *Proc. 3rd Int. Conf. on Light Scattering in Solids (Rampinas, Brazil)* (Union of Pure and Applied Physics) pp 953-8
Ganesan S 1962 *Acta Crystallogr.* **15** 81-6
Hoffman S F and Szczepaniak 1979 *J. Magn. Reson.* **36** 359-70
Konstantinova V P, Sil'vestrova I M and Aleksandrov 1959 *Sov. Phys.-Crystallogr.* **4** 63-7
Rehwald W and Volanthen A 1980 *J. Phys.: Condens. Matter* **13** 3823
Winterfeldt V, Schanack G and Klopperpieper A 1977 *Ferroelectrics* **15** 21-34