

Neutron diffraction studies of the ferroelectric/paraelectric transition in triglycine sulphate

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Introduction

Triglycine sulphate (TGS), $(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4$ is a hydrogen-bonded ferroelectric with a Curie temperature, T_C , in the range 47 - 49°C [1]. The unit cell consists of three glycine molecules G1, G2, G3, and one sulphate ion. At room temperature (in the ferroelectric state) it exhibits a monoclinic structure ($a = 9.417$, $b = 12.643$, $c = 5.735$ Å and $\beta = 110.38^\circ$ [1]). The transition is generally classified as a continuous, second-order one of the order-disorder type, with the structure going from $P2_1$ to $P2_1/m$ with increase in temperature through T_C [2]. There is a large body of work in the literature on TGS, because of its applications in medicine and in bolometry. While the former is not related to its ferroelectric properties, the latter is and arises from the very large pyroelectric effect seen in TGS [3].

There have been a number of x-ray studies of the crystal structure of TGS [1-6]. In Figure 1,

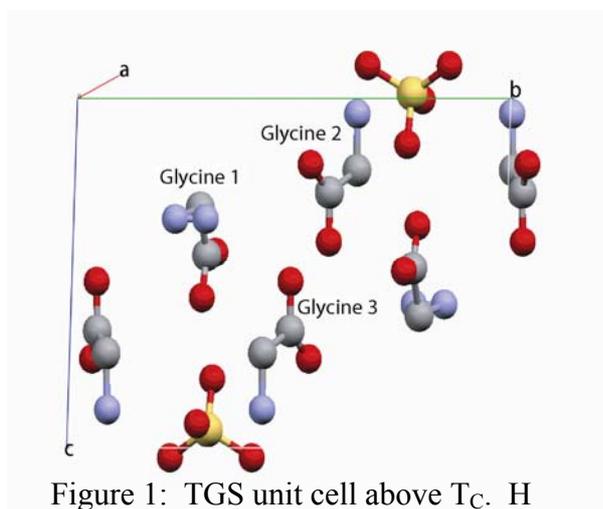


Figure 1: TGS unit cell above T_C . H atoms excluded.

an elevation of the crystal structure is shown (H atoms excluded). Above T_C there is a mirror plane through the sulphate and G1 molecules such that the G2 and G3 molecules are equivalent. The mirror plane running through the G1 molecule is purely statistical in that the NH_3 group of the molecule is disordered about the plane. There is a hydrogen bond joining G2 and G3 and the proton is dynamically disordered between two positions. On cooling through T_C the proton sits in one of the two positions, the glycine molecules move off symmetry and a spontaneous polarisation occurs.

A recent theoretical study [7], based on the available experimental data, indicated that the ferroelectric transition had its fundamental origins in the dynamic behaviour of the NH_3 group of G1, which moves in a double-well potential spanning the mirror plane through G1.

Experimental Details

The TGS crystals being used in this project were grown in a super-saturated aqueous solution of the components in stoichiometric molar ratio, held at constant temperature in a specifically

designed uniform temperature enclosure. Neutron data for a small irregularly shaped piece of crystal of approximate side length 1.5 mm were measured using the 2TANA single crystal neutron diffractometer at the High Flux Australian Reactor (HIFAR), Lucas Heights. Data sets were measured from 22°C to 69°C using the 2TANA cryofurnace, the temperature accuracy being $\pm 1^\circ\text{C}$. Data were collected over two experiments with no evidence of hysteresis as a function of temperature. Refinements were performed using the UPALS software and done in the space group $P2_1$, with two O atoms of the SO_4 ion and the U_{ij} of the G3 and G2 constituent atoms constrained as if in the $P2_1/m$ phase. These constraints were necessary to remove severe parameter correlations near to and above T_C . A summary of the refinements is given in Table 1.

Table 1 : R-factors, number of independent reflections and Parameters per refinement.

T(°C)	R1(%)	Rw(%)	N_{hkl}	N_{par}
22	6.1	14.7	2272	247
30	7.1	16.2	2312	247
35	6.9	15.8	2280	247
45	7.0	15.3	2303	247
50	6.3	13.7	2328	247
69	6.2	13.7	2333	247

The H atom between G2 and G3 and the NH_3 group of G1 were refined as disordered groups centered about the symmetry positions of $P2_1/m$ but with relative occupancies refined for the H atom and for the NH_3 group. From these refined occupation parameters, a long-range order parameter, S , was calculated according to

$$S = |p_1 - p_2| \quad (1)$$

where p_1 and p_2 are the occupation fractions for the two equivalent positions. Comparably defined order parameters were used to describe the disorder of the NH_3 group and the H atom. A similar description for the long-range order in TGS has been used previously by Itoh *et al.* [2]. Having the order parameter as a function of temperature, it is then possible to calculate a critical exponent β associated with the transition using the equation

$$S = c(T_C - T)^\beta \quad (2)$$

where c is a constant and T_C is the transition temperature.

Results

Well below the transition temperature the NH_3 group of the G1 molecule sits to one side of the $P2_1/m$ mirror plane which is perpendicular to and cuts the b axis at $1/4$. Also, the hydrogen atom between the G2 and G3 molecules is in one of two sites. The direction of polarization (in the $+b$ or $-b$ direction) is determined by which alternative position the NH_3 group and H atom occupies (see Figure 2a). As the temperature is increased, the NH_3 group of G1 and the H atom between G2 and G3 begin to flip between their two alternative positions, resulting in the occupancy of the alternative positions varying from 100% and 0% towards the 50% and 50% that exists above T_C (see Figure 2 b).

The critical exponent, β , from a fit to the measured polarization in TGS has been calculated to be 0.45 [8]. From the fitted curves (see Figure 3) to the temperature dependent order

parameters for $T < T_C$, critical exponents of 0.20 ± 0.06 and 0.32 ± 0.01 were calculated for the onset of disorder for the H atom between G2 and G3 and for the NH_3 about the mirror plane, respectively. Errors in the calculated exponents were found by substituting the lower and upper extreme values for the data sets and recalculating β . The fits to the exponent for the order parameter in each case also included the measured T_C for the present crystals, determined as the peak in the dielectric constant versus temperature studied using an Andeen-Haegerling capacitance bridge and an associated variable temperature capacitance probe, normally used as a capacitance dilatometer for thermal expansion measurements [9]. This result is shown as the insert to Figure 3. It should be noted that the ferroelectric transition in the present crystals is reversible.

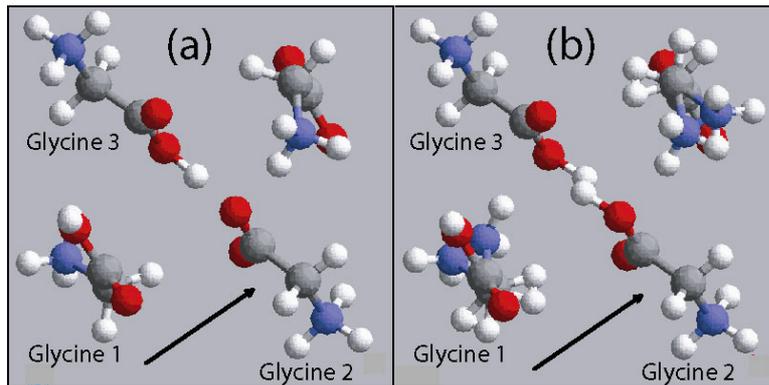
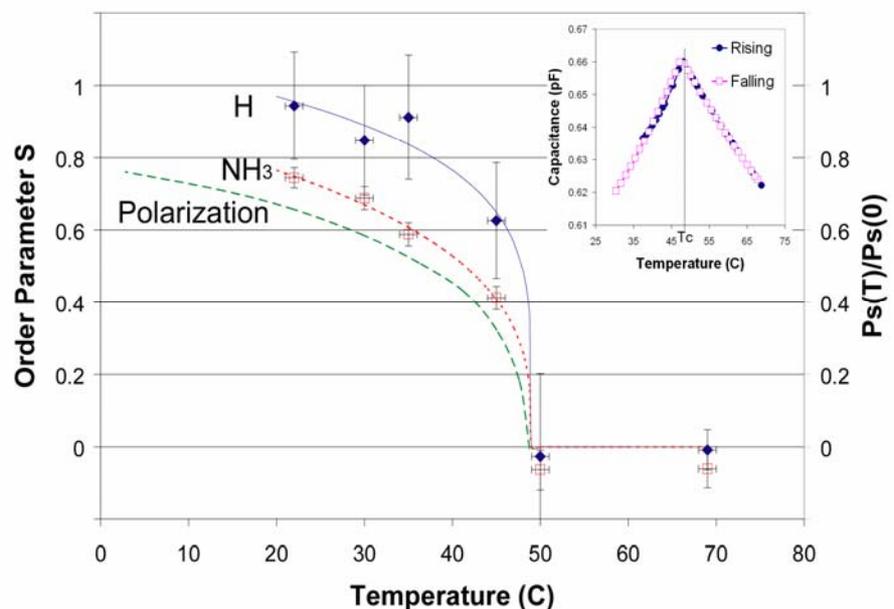


Figure 2: Refined structures looking down the a direction for, (a) well below T_C and, (b) above T_C . The arrows in the figures indicate the polarisation, or b , direction.

Figure 3: Calculated order parameters for both the disordered H atom between G2 and G3, (filled circles), and the disordered NH_3 group of the G1 molecule (open squares). The solid and short-dashed lines are least-squares fits of equation (2). The long-dashed line is the bulk polarisation of TGS [8]. Insert shows the measured capacitance with TGS as the dielectric, as a function of temperature, showing T_C and the reversibility of the transition.



Discussion

It would appear from Figure 3 that the ordering of the H atom between G2 and G3, and the ordering of the NH_3 group of G1 are not directly coupled together. While the trends in the two values are similar, the disordered H atom appears to have a stronger tendency to sit in the

one site compared to the other, than that of the NH₃ group at the same temperature. This tendency is shown clearly in the refined critical exponents, β , for the two order parameters. β for the disordered NH₃ group is approximately 0.12 higher than that for the disordered H atom. These results appear to contradict a previous theory which suggested the flipping of the NH₃ group directly caused the H atom between G1 and G2 to switch positions [10].

Also apparent from Figure 3 is the fact that the position of the NH₃ group has a greater contribution to the spontaneous polarization of the bulk crystal than that of the disordered H atom. However it is also apparent that there must be other factors influencing the total polarization of the crystal, as the order parameter for both the H atom and NH₃ group tend towards unity at higher temperatures than the polarization. Itoh *et al.* [2] have shown that the order parameter for the NH₃ group is in fact unity at approximately -150°C. The result of this tendency is a significantly lower β value calculated for the disordered H atom and NH₃ group, than that for the measured polarization.

Conclusion

The structure of TGS around its paraelectric to ferroelectric transition has been investigated. It has been shown that the structure well below the T_C is P2₁, with the NH₃ group of G1 and the H atom between G2 and G3 fixed in one of their two possible positions. As T_C is approached from below, the NH₃ and the H atom begin to jump between their two possible positions with increasing probabilities. Once T_C is reached there is equal probability of the NH₃ group and the H atom occupying each of their equivalent sites. This creates two statistical mirror planes within the unit cell and thus the space group above T_C is P2₁/m. It has been shown by defining a statistical order parameter that the flipping of the NH₃ group and the H atom are not directly correlated. Also it appears that the onset of the disorder of neither the NH₃ group nor the H atom will fully account for the temperature dependence of the polarization.

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