Mössbauer Investigation of Iron-doped Triglycine Sulphate

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A Mössbauer investigation of iron-doped triglycine sulphate (tgs) has been made in order to investigate the changes occurring at the iron nuclei as the properties of tgs change with temperature. Variations in the Mössbauer spectra at temperatures above the normal Curie point for undoped tgs (49 °C) have been correlated with the behaviour of polarisation–voltage hysteresis loops for the iron-doped material. The loops persist above T_c and continue to show asymmetry up to 60 °C. Above this temperature an anomalous increase in Mössbauer quadrupole splitting occurs. On cooling the specimens from 60 °C to below 49 °C the loops reappear but show no bias; bias is gradually restored over a period of hours. Similarly, the quadrupole splitting does not decrease immediately the temperature is lowered, but only after a similar period of time has elapsed. These results are discussed and possible mechanisms for the internal bias field are suggested.

TRIGLYCINE SULPHATE (tgs) is a ferroelectric material that normally shows a polarisation response which is symmetrical with respect to the sense of the applied voltages. It has been shown that crystals grown in the presence of Fe^{3+} give an asymmetric polarisation response, that is the ferroelectric hysteresis loops are displaced with respect to the polarity of the applied voltage,[1] and the crystals are said to be ' biassed '. It was suggested that the Fe^{3+} occupies a crystallographic site between the GII and GIII glycine–glycinium groups in tgs [1] (Figure 1). Confirmation for this postulation comes from a study of copper- and chromium-doped tgs.[2,3] In the latter case, it was found by e.s.r. spectroscopy that the ligands surrounding Cr^{3+} moved in one direction or the opposite depending on the sign of the applied electric field.[3]

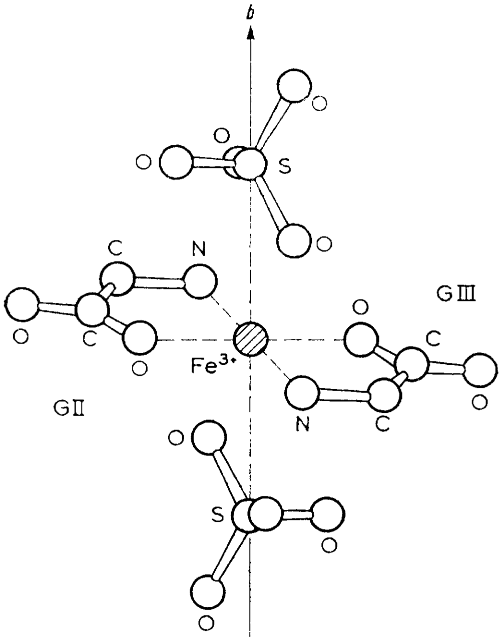

FIGURE 1 Proposed six-co-ordinate structural environment of Fe^{3+} in doped tgs, showing the *b* axis

This paper reports the results of Mössbauer studies on iron-doped tgs which were made in order to investigate the co-ordination of the iron(III), and to determine the changes that may occur on traversing the Curie temperature (which for undoped tgs is 49 °C). The results described help to explain the bias effects observed for this material.

EXPERIMENTAL

The crystals of triglycine sulphate were prepared by conventional slow-cooling growth from an aqueous solution of tgs containing 3 mol dm^{-3} $FeCl_3$.[1]

The Mössbauer apparatus [4] consisted of an Elscint MD3 spectrometer and a Nuclear Data ND2200 multichannel analyser. The constant-acceleration spectrometer could be operated in a sawtooth- or triangular-waveform mode, the latter giving two sets of data for each spectrum from the positive and negative halves; these halves could be folded together, doubling the total number of counts for improved statistical accuracy. Low-temperature measurements were made in a Ricor MCH5 cryostat; temperatures were measured to ± 1 K, and regulated by a Ricor TC4B coolant gas-flow controller to better than ± 0.2 K. The source was *ca.* 1 mCi ^{57}Co in palladium. The solution absorbers were sealed in 5-mm thick poly(methyl methacrylate) holders with thin windows of the same material, and were quick-frozen before being placed in the cryostat. The solid absorber material did not contain large enough crystals for single-crystal studies and so was roughly powdered (so that the particle size was highly non-uniform) and sealed in lead rings with Sellotape; the absorber thickness was *ca.* 0.2 g cm^{-2}. Velocity calibrations were made by using thin (10 mg cm^{-2}) high-purity iron foils. All isomer shifts were referred to natural iron as the zero point. All spectra were analysed by a simple non-linear least-squares fitting program, run on the Imperial College CDC6400 computer.

RESULTS AND DISCUSSION

The Mössbauer data obtained are in the Table. A frozen solution of $FeCl_3$ in water gave a single-line spectrum. The solution was yellow in colour. When glycine was added the colour changed to red-brown, suggesting that complex formation had occurred.[1] The Mössbauer spectrum for this solution when frozen showed a quadrupole splitting and change in the isomer shift, indicating that the Fe^{3+} was in a new environment,

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[1] J. Silver, E. A. D. White, and V. M. Wood, *J. Materials Sci.*, 1975, **10** 2010.

[2] S. Hoshino, Y. Okaya, and R. Pepinsky, *Phys. Rev.*, 1959, **115**, 323.

[3] A. Lösche and W. Windsch, *Phys. Stat. Solidi*, 1965, **11**, 455.

[4] B. L. Dickson and L. V. C. Rees, *J.C.S. Faraday I*, 1974, 2038.

thus confirming the formation of a stable complex. The addition of sulphuric acid to the solution at this stage caused a slight increase in the isomer shift, and the quadrupole splitting was reduced, suggesting that the co-ordination of the Fe^{3+} was modified either by the presence of $[SO_4]^{2-}$, or simply from the lower pH: the former is more likely in view of refs. 1—3. The quadrupole splitting for this frozen solution was similar to that for the tgs crystals doped with Fe^{3+} at 80 K. No spectra were obtained from solutions at 295 K, obviously due to the low recoilless fraction in solution at this temperature. These results confirm that the Fe^{3+} detected is present within the tgs lattice in the powdered crystal studies, and is not present as solvent inclusions, since the spectra would disappear when the inclusions became liquid at temperatures above *ca.* 270 K. The results also indicate that the Fe^{3+} in the lattice is co-ordinated to both glycine and sulphate groups, which is consistent with the placing of Fe^{3+} between the GII and GIII units. The fact that the isomer shift was increased in the frozen-solution spectra compared with that of the crystals at 80 K may indicate that the electron density of the Fe^{3+} in the frozen solution is greater because the molecule is isolated.

Mössbauer data (mm s^{-1}) for iron-doped tgs

Sample	T/K	Chemical shift	Quadrupole splitting	Linewidth
$FeCl_3$ *	80	0.803 ± 0.007		0.559 ± 0.01
$FeCl_3$ + Gly *	80	0.766 ± 0.004	0.899 ± 0.006	0.221 ± 0.005
$FeCl_3$ + Gly * + H_2SO_4	80	0.788 ± 0.003	0.646 ± 0.003	0.201 ± 0.005
Iron-doped tgs	80	0.542 ± 0.003	0.598 ± 0.006	0.23 ± 0.01
	180	0.493 ± 0.007	0.706 ± 0.006	0.26 ± 0.02
	315	0.419 ± 0.007	0.687 ± 0.008	0.26 ± 0.03
	325	0.413 ± 0.007	0.684 ± 0.008	0.24 ± 0.02
	335	0.408 ± 0.009	0.678 ± 0.009	0.25 ± 0.02
	345	0.394 ± 0.005	0.718 ± 0.005	0.260 ± 0.005
Iron-doped tgs after heating	330	0.413 ± 0.005	0.720 ± 0.005	0.274 ± 0.005
	315	0.419 ± 0.005	0.708 ± 0.005	0.267 ± 0.005

* Frozen-solution experiment.

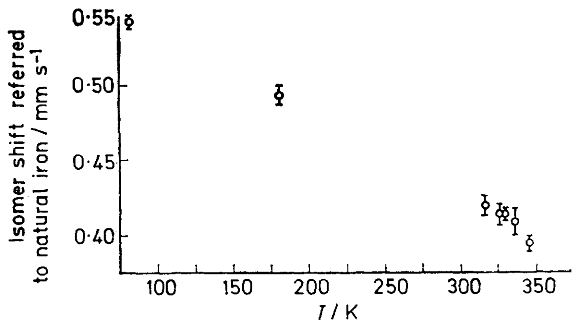

FIGURE 2 Mössbauer isomer shift plotted against temperature for iron-doped tgs

On studying the spectra of crystals heated from 80 to 345 K, at various temperatures (Table), the isomer shift was found to be a maximum at 80 K and steadily decreased as the temperature increased (Figure 2). This is a second-order Doppler effect. The quadrupole splitting was smallest at 80 K, increased to 0.706 mm s^{-1} at 180 K, and then decreased as the Curie point was reached. The maximum at 180 K occurs at a temperature where the polarisation of tgs is also very large.[5] Above the Curie point the quadrupole splitting again became larger. This final increase in the splitting took place between 335 and 345 K on heating the specimen, but it did not disappear on cooling again until 315 K (Figure 3). This behaviour, indicative of a structural hysteresis effect on temperature cycling, was also observed during studies of the polarisation–field loops for tgs–Fe cycled through the Curie point (Figure 4). These hysteresis loops persisted at temperatures above the normal Curie point on the heating cycle; the loops disappeared at *ca.* 60 °C and did not reappear on cooling until *ca.* 49 °C, when they displayed the appearance characteristic of undoped tgs. The return of the bias displacement took several hours and was apparently a function of time and temperature below the Curie point.

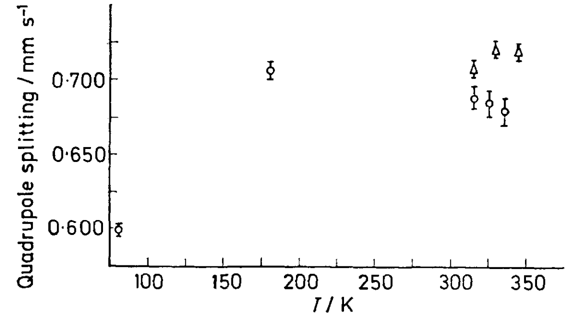

FIGURE 3 Quadrupole splitting plotted against temperature for iron-doped tgs: (○), heating cycle; (△), cooling cycle

It is clear that the disappearance of the bias is associated with an increase in quadrupole splitting, and this must be interpreted as a change in the co-ordination geometry of the ligands surrounding the Fe^{3+}. Either the iron(III) chelate is hydrogen bonded to the surrounding lattice or it is distorted by the bias field. When the bias decreases to zero the hydrogen bonds either break and allow the chelate to resume its natural configuration, or the distortion caused by the field ceases with the same effect, which is seen by an increase in the quadrupole splitting above the Curie point. It is known that in tgs doped with Cr^{3+} the ligand geometry changes according to the applied external field.[3] In material doped with Fe^{3+} the presence of the Fe^{3+} induces bias indicative of long-range order; the fact that the quadrupole splitting changes above the Curie point is consistent with the disappearance of such ordering, below the Curie point, which determines the position of the iron(III) chelate group. The hydrogen bond between GII and GIII is thought [6] to take part in the biassing mechanism; the iron(III) chelate substitutes for a GII and GIII pair and it is possible for the chelate to hydrogen bond to the next glycinium ion (II/III) causing long range changes since

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[5] D. J. White and H. H. Wieder, *J. Appl. Phys.*, 1963, **34**, 2487.

[6] N. Nishimura and T. Hashimoto, *J. Phys. Soc. Japan*, 1973, **35**, 1699.

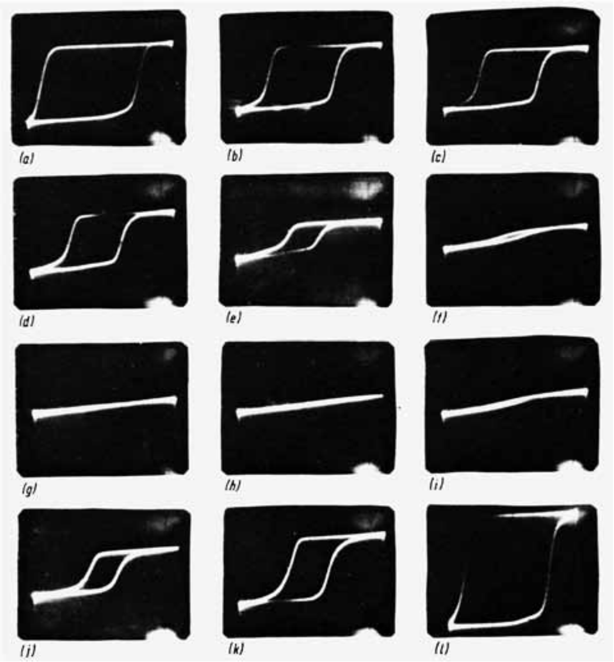

FIGURE 4 Polarisation–voltage hysteresis loops for ion-doped tgs on heating [(*a*)—(*g*)] and subsequent cooling [(*h*)—(*l*)]. Respective temperatures were: 21 (*a*); 43 (*b*); 46 (*c*); 49 (*d*); 56 (*e*); 58 (*f*); 59 (*g*); 49 (*h*); 48 (*i*); 46 (*j*); 43 (*k*); and 21 °C after 24 h (*l*). The loss of loop symmetry in (*j*) and (*k*) is to be noted

the chelated glycine bonds will be electronically different from normal glycine. The glycine in the metal chelate can then cause the bias field, modifying the hydrogen-bond system throughout the tgs and aligning the $[NH_3]^+$ group on GI with the field. Alternatively, the SO_4 groups around the iron(III) chelate may be drawn out of position by the Fe^{3+}, which would cause similar effects on the hydrogen-bonding network of tgs. This would strain the tgs lattice and explain why only small amounts of metal dopant are incorporated.

The broad lines recorded in the Mössbauer spectra for iron-doped tgs may indicate the presence of two iron(III) sites: the first as in Figure 1, and the second with both of the glycine groups in the *cis* rather than in the *trans* configuration. The latter would not fit into the lattice readily, but this does not eliminate the possibility. Additionally the sulphate ions may be partly replaced by Cl^-, which would add to the line broadening. However, the Mössbauer spectra were not fitted for more than one type of site since no other physical evidence for such site modifications has been obtained.

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