

Time-resolved Neutron Diffraction Studies: The Ferroelectric Transition in Triglycine Sulphate

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A stroboscopic technique has been developed enabling the real-time response of neutron Bragg reflections to be monitored during the application of high-voltage fields to a crystal. The real-time responses of reflections from triglycine sulphate at temperatures in the vicinity of its ferroelectric/paraelectric transition show some unusual properties. Some of the recent data from these experiments are presented together with a discussion of the physical mechanisms leading to changes in Bragg reflection intensities.

1. Introduction

Time-resolved studies of diffraction intensities are essential for an improved understanding of the kinetics of phase and structural transitions in crystalline solids. The bulk penetration of neutrons into materials makes them ideal as a probe but the incident neutron flux required to generate diffraction intensities as a function of time during a single transition needs to be large, especially if one wishes to observe changes over microsecond time scales. However, such problems can be overcome and diffraction intensities collected with very good timing resolutions, if the transition is reversible. Stroboscopic techniques are those in which a reversible transition is driven repetitively by a cyclic perturbing field, for example, as in the case of a crystal undergoing a ferroelectric/paraelectric transition in response to an applied electric field [1]. The detected neutrons are time-stamped and binned according to the time at which they were diffracted by the crystal during the perturbing field cycle, thereby improving the statistics for the peak intensity as a function of time during each cycle.

Triglycine sulphate (TGS [(NH₂CH₂COOH)₃H₂SO₄]) is a hydrogen-bonded ferroelectric with a $T_C \sim 322\text{K}$ [2]. 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. The transition is a continuous (second-order) one of the order-disorder type, with the structure going from $P2_1$ to $P2_1/m$ on heating through T_C [3]. During the application of electric fields of sufficient strength, at temperatures close to T_C , the crystal will be driven to the completely ordered ferroelectric state.

2. Experimental Details

The instrumentation, developed on The Australian Strain Scanner (TASS) at the Lucas Heights HIFAR research reactor, has been described in detail elsewhere [4]. The neutron detector on the instrument is a 30-line, position-sensitive detector which, when set for best angular resolution, collects data over a 2.24° angle to $\pm 0.7^\circ$ accuracy. Timing resolution was approximately $15\mu\text{s}$. A simple, variable-temperature chamber, incorporating a Peltier module suitable for the range 273 to 340K, was constructed to contain the crystal on a three-circle goniometer. Temperature measurement and control to approximately $\pm 0.05\text{K}$ were accomplished using a Lakeshore temperature controller.

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The TGS crystals were grown from super-saturated aqueous solutions of the components in stoichiometric molar ratio, held at constant temperature in a crystal-growth enclosure. Each crystal was aligned, cut to the required size and mechanically polished perpendicular to its polarization [010] direction. The final dimensions of the particular crystal employed for the results reported here, were 4.25mm x 2.85mm x 18mm, the 2.85mm dimension being the polarization direction. Silver electrodes were painted on to the (0k0) surfaces using a commercial, conductive, silver paint. A capacitance measurement reported elsewhere [5] showed the transition to be reversible with a T_C of 322K.

3. Results and Discussion

Various dynamic effects to the diffracted intensity have been observed during the application of square electric-field waveforms. The integrated intensities of the (060) Bragg peak in TGS at various frequencies and at a sample temperature of 324.5K, are shown in Fig. 1. At low frequencies the intensities of the peak in the dynamic field-on and field-off states are very close to the static field-on and field-off intensities. As the frequency is increased the field-on intensity initially falls until at high frequencies the total diffracted intensity throughout the applied field waveform is reduced. Relaxation effects were observed after the release of the electric field at all frequencies, but the degree of these effects varied greatly with experimental conditions. Fig. 2 shows the frequency dependence of the relative intensity difference between the field-on and field-off states of the waveform at various temperatures, showing that the intensity difference observed between the field-on and field-off states approached zero at high frequencies.

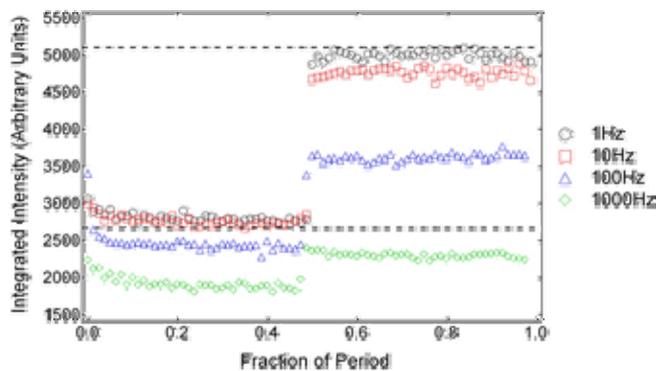


Fig. 1. Time variation of integrated intensity of the (060) peak in TGS (at 324.5K) during the application of electric fields at four different frequencies. Upper and lower dashed lines indicate the static field-on and field-off intensities, respectively.

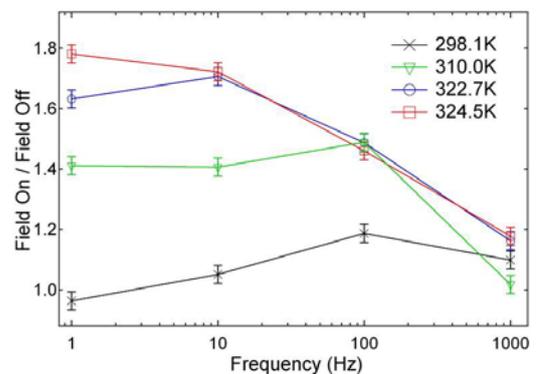


Fig. 2. Frequency dependence of the relative intensity between field-on and field-off conditions for the (060) peak from TGS at various temperatures.

Some of the most interesting data have been collected over short time scales where the Bragg intensities show “spikes” at both field-on and field-off conditions. Fig. 3 shows the response of the (060) peak during the application of a unipolar, positive, electric-field waveform, with field-on being the first half of the cycle. The effect of changing the polarity of a unipolar field was small although similar “switching spikes” in the intensity were observed. Application of a bipolar field led to a suppression of the intensity “spikes” at the changes in field amplitude (Fig. 4). This is an important observation as it suggests that the “spike” in intensity is associated solely with the transition between field-on to field-off states.

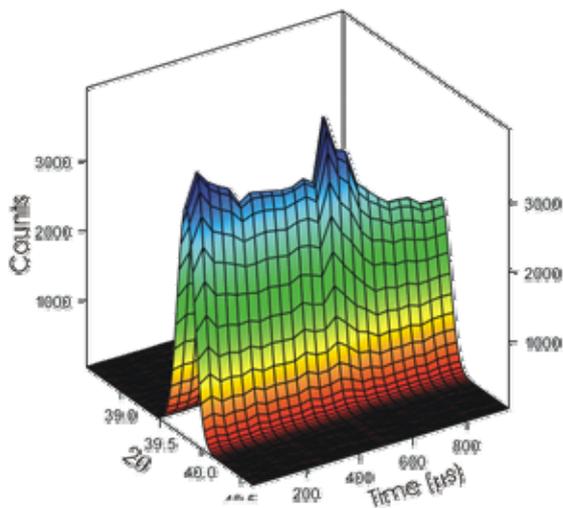


Fig. 3. The (060) peak from TGS (at 323K) during the application of a 1kHz, unipolar, positive, square wave. Field-on is for the first half of the cycle.

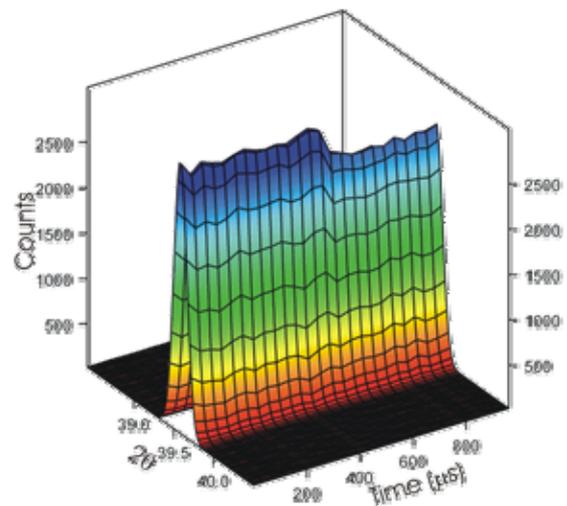


Fig. 4. The (060) peak from TGS (at 323K) during the application of a 1kHz, bipolar, square waveform. Field positive is for the first half of the cycle.

It is obvious that such intensity changes are related to changes in extinction conditions of the crystal caused by fluctuations in the crystal (domain walls, strain, critical scattering effects, etc.) associated with the transition. Such reductions in extinction have been observed for other materials which undergo order/disorder transitions [6-8]. To this end an ongoing experiment is currently being undertaken at the triple-axis instrument, PUMA, located at the FRM2 reactor in Munich, Germany.

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References

- [1] G. Eckold, M. Hagen and U. Steigenberger, *Phase Transitions* **67**, 219 (1998).
- [2] S. Hoshino, Y. Okaya and R. Pepinsky, *Phys. Rev.* **115**, 323 (1959).
- [3] K. Itoh, A. Nishikori, H. Yokomizo and E. Nakamura, *Jap. J. Appl. Phys.* **24**, 594 (1985).
- [4] J.E. Daniels, A.J. Studer, T.R. Finlayson and M.E. Hagen, in *Physics for the Nation* (Proceedings of 16th National Congress of the Australian Institute of Physics) (Canberra, A.C.T., Australia) 31 January – 4 February, 2005. ed. M. Colla, ISBN 0-9598064-8-2 (Australian Institute of Physics, 2005) Paper No. CMMSP MOC 34.
- [5] J.E. Daniels, R. Piltz, M.E. Hagen and T.R. Finlayson, *ibid.*, Paper No. CMMSP PTU 86.
- [6] G.E. Bacon and R.S. Pease, *Proc. Roy. Soc. A* **230**, 359 (1955).
- [7] J. Joffrin, U.T. Höchli, M. Maglione, C.M.F. Zeyen and J.L. Soubeyroux, *Physica B* **156-57**, 88 (1989).
- [8] S. Asbrink and S-H. Hong, *Nature* **279**, 624 (1979).