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Effects of γ-Irradiation on Tri-Glycine Sulfate†

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Abstract—The effects of γ-irradiation below the Curie point on the ferroelectric tri-glycine sulfate (TGS) were examined. Principal among these effects is the change, as a function of radiation dose, of the energy absorbed by a sample in going from the polar state to the non-polar state. This energy was found to be 0.73 cal/g for a virgin sample and 0.44 cal/g for a sample irradiated to 5×10^6 r. The shift of the Curie point toward lower temperatures ($\sim 5°$ C for 5×10^6 r) was found in the specific heat measurements as well as in the electrical measurements. The internal bias which appears in the hysteresis loops of irradiated samples was studied as a function of temperature, sample thickness, and time of application of the a.c. measuring field. Both the internal bias and the coercive field exhibit a linear increase with increased γ-ray dose.

Introduction

Since the investigations carried out by Chynoweth[1] in 1959 on x-radiation damage in tri-glycine sulfate (TGS) an increasing number of papers have appeared on this subject.[2–6] In the present investigation, we have measured the effects of γ-irradiation on the specific heat anomaly of TGS. When samples of TGS are irradiated below the Curie temperature, changes are seen in the ferroelectric hysteresis loops and the polar-axis dielectric constant. The hysteresis loops exhibit a bias, after irradiation, and the position of the dielectric constant anomaly shifts in temperature as does the specific heat anomaly. The starting material for both the electrical measurements and the specific heat measurements was the same crystal of TGS.

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Experimental Procedure

Samples (about 0.3 cm × 0.3 cm × 0.1 cm) for the electrical measurements were cut from a single crystal of TGS which was donated by Dr. S. Triebwasser of the IBM Research Center. Two opposite faces of each piece were coated with silver paint; each piece was then sandwiched between aluminum foils and placed between the electrodes of the measuring circuit. The crystals were contained in a cell which was provided with a heater and thermocouple so that the crystal temperature could be changed and measured. A Sawyer and Tower circuit,[7] with phase compensation, was used for displaying the hysteresis loops. Photographs were taken of the oscilloscope traces at each of the temperatures reported. The a.c. voltage at these points was kept on for a very short time to avoid "a.c. annealing". The irradiation facility for this part of the experiment was a 2000 curie Co^{60} source with a dose rate of 0.77×10^6 r/hr.

The specific heat anomaly was measured by using a micro-calorimeter[8] having linear temperature rise. In each case the sample was powdered TGS ~0.13 g, which was packed tightly into a copper capsule. Since the micro-calorimeter was of the differential type, an inert dummy was made up to match closely the heat capacity of the sample and its container over the range of temperature of interest. This dummy was a capsule, identical to that of the sample, containing sufficient iron filings to duplicate the thermal capacity of the sample and its container at room temperature. This procedure assured that any differences between the sample and dummy were small compared to the anomaly being measured. Each experimental run of the micro-calorimeter was calibrated by comparison with a small mass (~3 mg) of Rose's metal which, in turn, was calibrated with a small amount of pure gallium. Temperature rises of about 0.4° C/min were used. Other rates of temperature rise were used and the positions of the peaks of the specific heat anomaly were compared. The peaks did not shift and it is concluded that there were no significant differences in thermal conductivity of the sample as a function of irradiation.

The irradiation facility used for this part of the experiment was a Co^{60} source whose dose rate was 1.0×10^6 r/hr. In series A of runs the same sample of TGS was irradiated in increments of $\frac{1}{2}$ hr or 1 hr and measured after each incremental dose to achieve the total dose while in series B several samples were irradiated to the total dose reported.

Hysteresis loop observations in irradiated TGS show that, if the sample is irradiated without any previous electrical or thermal treatment, double loops appear. These loops are equally and oppositely displaced along the electric field axis but their relative size varies, in general, from case to case. If, before irradiation, the sample is heated through the Curie point and then cooled slowly the irradiation gives rise to two, equal sized, loops. If a very strong, external d.c. field is applied to the sample for a long time before irradiation, or during irradiation, the original hysteresis loop does not split but is displaced. The direction of displacement depends on the direction of the external field. There are some differences in the behavior of the internal bias of single and double hysteresis loops. All of the results on hysteresis loops given here refer to double loops unless otherwise specified. In addition, these loops are assumed to be symmetric along the electric field axis.

Results

For γ-ray doses up to 3×10^6 r, the increase of internal bias was nearly linear, the increase being 1.4×10^{-3} V/cm/r. The change of the coercive field also showed a linear dependence on dose with an increase of 2.1×10^{-4} V/cm/r. These results are in good agreement with previous data.[4]

The internal bias in single loops showed a temperature dependence similar to that found for Rochelle salt.[9] In Rochelle salt the internal bias is nearly constant at temperatures near the lower transition point and drops off near the upper transition point. In double loops, however, the internal bias varies in a manner similar to that observed for spontaneous polarization;[10] becoming unobservable at temperatures greater than the Curie point, T_0.

Figure 1 is a plot of this behavior for a sample irradiated to 3×10^6 r. The applied voltage was the same at each temperature and between each measurement the voltage was turned off to avoid "fatigue"

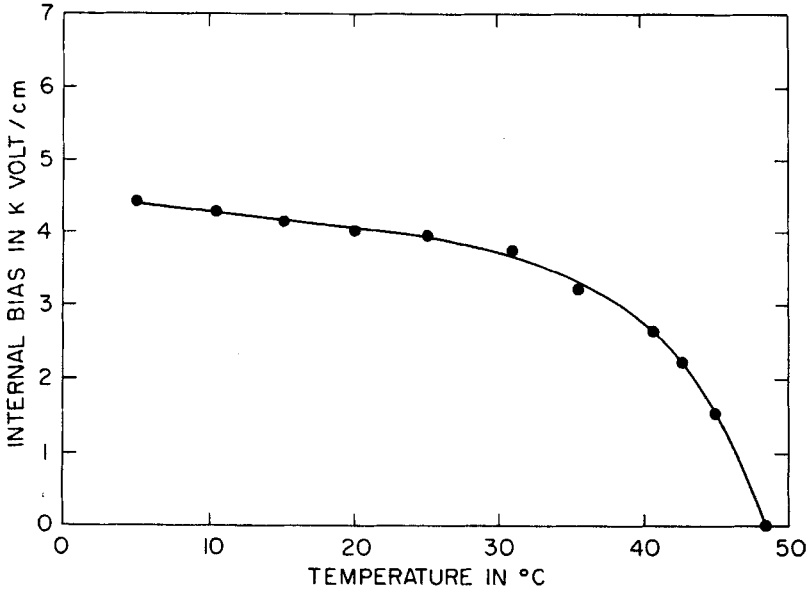

Figure 1. Behavior of internal bias as a function of temperature for a sample exhibiting a split hysteresis loop. Dose was 3×10^6 r.

of the hysteresis loops. There is an effect which tends to decrease the bias with increasing time of application of the sweeping voltage ("a.c. annealing"). Only a few seconds were necessary to take the photograph at each temperature. Figure 2 shows a series of photographs of the double loops at different temperatures.

As already mentioned, the double loops of γ-irradiated TGS crystals showed "a.c. annealing". This appeared as a sliding together of both halves of the double loop under the influence of the externally applied a.c. field. This phenomenon was also observed by Chynoweth,[1] in the X-ray investigation, after short periods following the irradiation. In the present case partial "a.c. annealing" was observed in many samples even after the

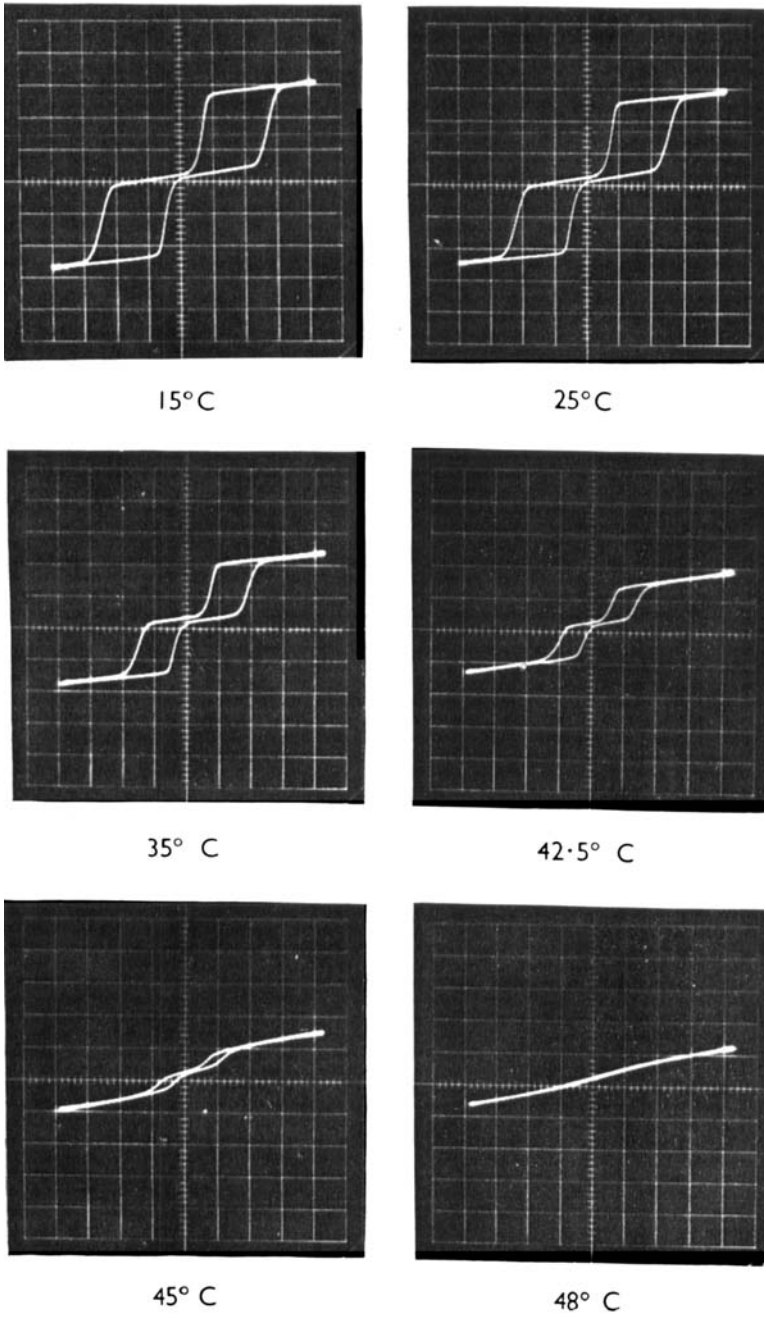

Figure 2. Oscilloscope traces used to obtain the points for Fig. 1.

samples had sat at room temperature for several weeks after irradiation. The internal bias appeared to consist of a permanent portion, which remained unchanged several hours after the application of the a.c. field, and an "annealable" part which decreased exponentially in about 5 min. Figure 3 shows the variation of the internal bias, at room temperature, with time of applied a.c.

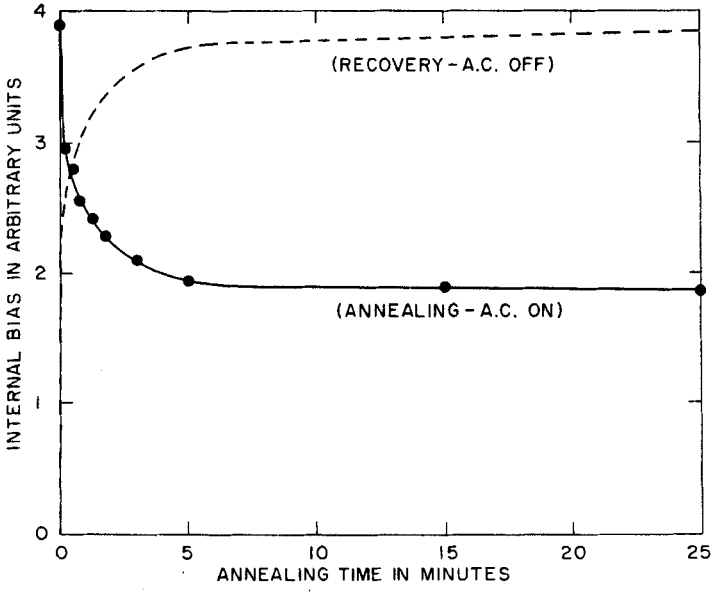

Figure 3. Internal bias as a function of time of application of a.c. measuring field. Measurements were at room temperature on a sample irradiated to 3×10^6 r. Amplitude of measuring field was 13.5 KV/cm. The dashed line represents the average of experimental points taken during the recovery of the internal bias.

field (13.5 kV/cm). The recovery of the initial value, once the a.c. field has been turned off, takes place in approximately the same manner as the annealing; it is initially very rapid, then approaches the initial value asymptotically. Several pictures taken at different times during the annealing process are reproduced in Figure 4. The amplitude of the external a.c. field influenced somewhat the life-time of the process, faster annealing being produced by stronger

amplitudes. Observations of the internal biasing field with several samples of different thickness showed an approximately constant value for crystals receiving the same radiation dose. In addition,

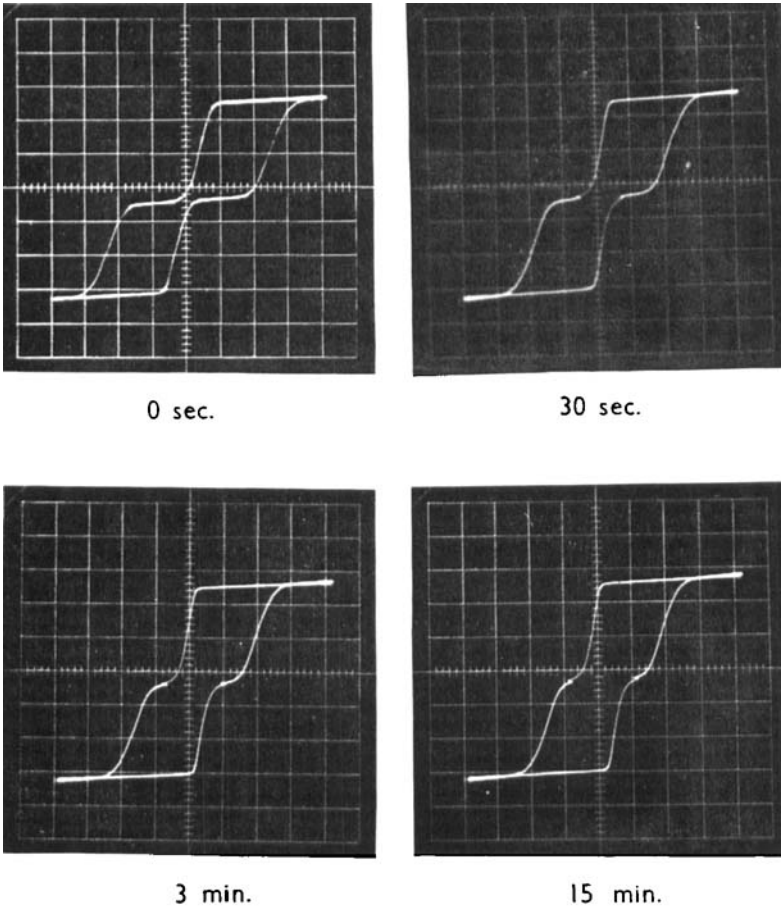

Figure 4. Oscilloscope traces which were used in obtaining the points for Fig. 3.

irradiating a thick crystal and diminishing the thickness of it (by cutting or grinding) produced the same effect.

Figure 5 shows replicas of recorder traces of calorimetric measure-

ments on a virgin sample and a sample irradiated to 5×10^6 r. The base line is determined by extending the linear portions before and after the anomaly. The area between the base line and the curve for the virgin sample corresponds to 0.71 cal/g and the area for the irradiated sample corresponds to 0.44 cal/g. It must be pointed out that in the actual trace, the straight portions used to determine the base line are of the order of 6 in. or longer. The rise of the trace between 0° C and 5° C is inherent in the calorimeter. In

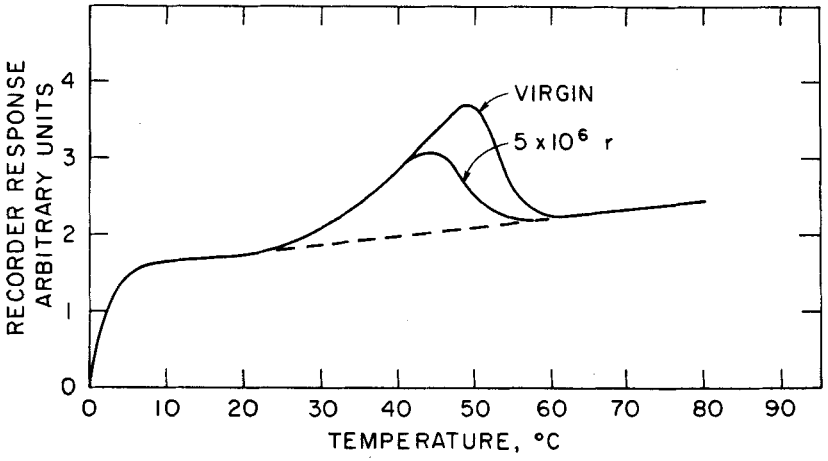

Figure 5. Reproduction of recorder trace for specific heat anomaly measurements. Temperature increase was about 0.4° C/min.

Figure 6 are the results of the energy anomaly as a function of dose. Those points marked with a circle are for series A and those marked with × are for series B. Although for each measurement the temperature of the sample was raised to about 125° C, there appears to be no substantial annealing of the radiation induced damage since the two sets of points follow approximately the same behavior. A further check of the change of the anomaly was made by replacing the inert dummy used in all of the above measurements. For this differential measurement one side of the calorimeter contained a virgin sample and the other side contained an equal amount of TGS irradiated to 5×10^6 r. The measured energy

difference was 0.31 cal/g which is very close to the difference shown in Figure 6. Since the sample powders had effectively the same surface area this last check also served to eliminate the possibility of the effects of adsorbed gases on the measurement of the samples in the previous runs. The energy anomaly for a virgin sample reported here falls between the value of 0.50 cal/g of Hoshino, *et al.*[10] and the value of 1.07 cal/g of Strukov.[11]

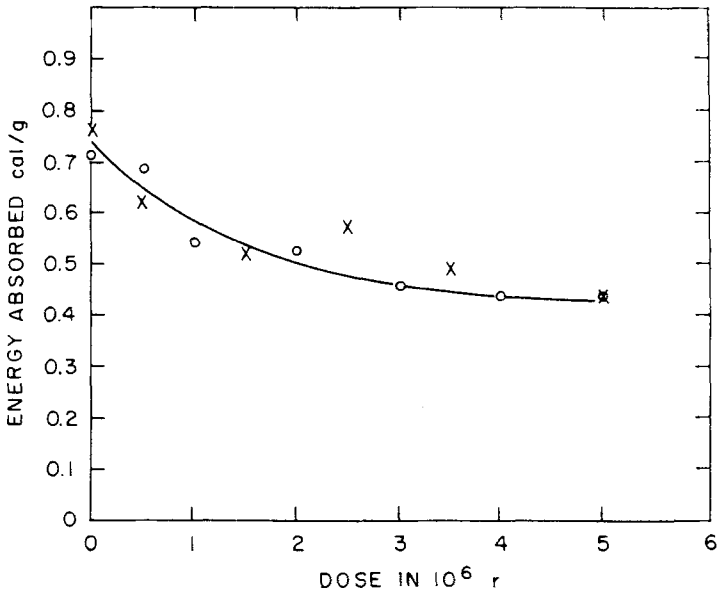

Figure 6. Energy absorbed by TGS sample as a function of γ dose. Open circles are for series A and × 's are for series B. See text for series A and series B conditions.

It was difficult to determine accurately the shift of the transition temperature, particularly in the irradiated samples, due to the broad peak of the response of the calorimetric measurements. Figure 7 shows the temperature shifts along with the shifts determined from measurements of the dielectric constant. For virgin samples the error in determining the temperature of the peak on the calorimetric measurements is about $\frac{1}{4}$ degree while in the case of

samples irradiated to 5×10^6 r the error is about 1 degree. Temperature shifts for series A of calorimeter runs are shown by open circles, series B by $\times$, and from the dielectric measurements by closed circles. The temperature shifts of the transition temperature reported here are in good agreement with those of Yurin, *et al.*[4] but

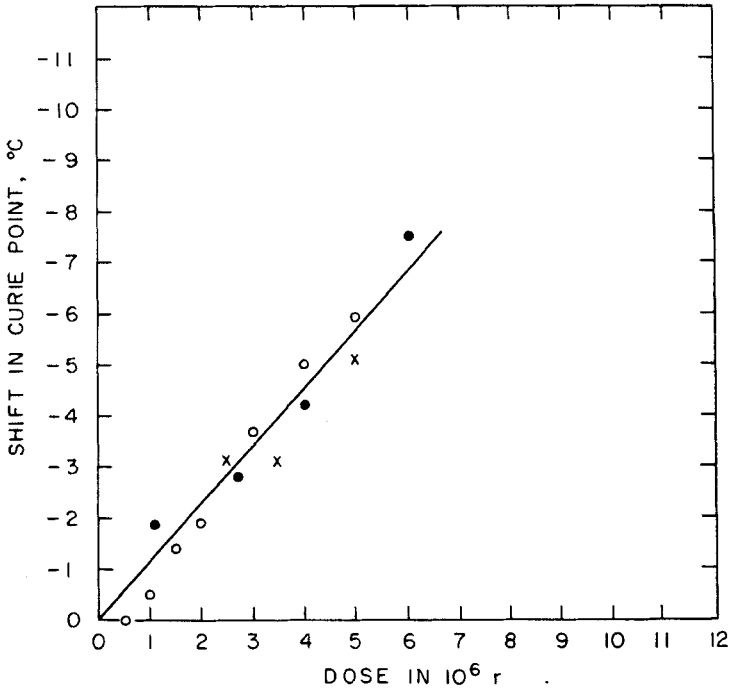

Figure 7. Shift of Curie point as a function of γ-dose. Open circles are for series A of calorimeter runs, $\times$ for series B, and solid circles are for dielectric measurements.

are considerably greater than those of Hilczer and Jaskulski[12] who report a shift of about 2.3° C for a dose of 5×10^6 r at a dose rate of 1.5×10^5 r/hr.

The points on Figure 7 referring to dielectric data were taken from measurements of the dielectric constant as a function of both temperature and irradiation as shown in Figure 8. Using the data of Figure 8, if one plots the reciprocal of the dielectric constant vs.

temperature, one obtains a series of straight lines that are parallel except at temperatures very near to the Curie point. The slopes of these lines yield the Curie constant of 3200° K and show the value

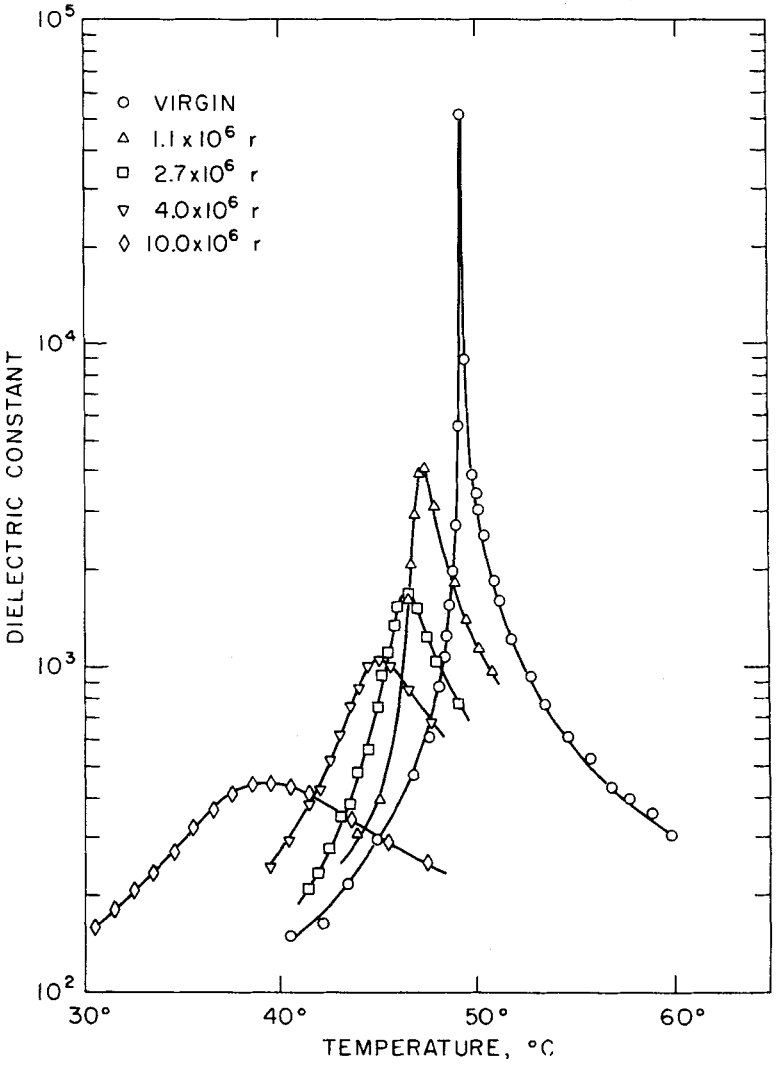

Figure 8. Dielectric constant as a function of temperature. No d.c. field for compensating the internal bias was used for these measurements.

of the Curie constant does not change with irradiation. It has recently been found that, if the dielectric constant is measured in the presence of a d.c. field to compensate for the internal bias, the curves, as shown in Figure 8, all come to a sharp peak.[13] Further, a plot of the reciprocal of the dielectric constant vs. temperature obtained by this type of measurement yields a straight line all the way to the Curie point for irradiations up to 10×10^6 r.

Discussion

The general expansion for the energy, A, in terms of the polarization, P, is given by

$$A = \tfrac{1}{2}\chi P^2 + \tfrac{1}{4}\xi P^4 + \tfrac{1}{6}\zeta P^6 + \qquad (1)$$

For a virgin sample of TGS we have, according to reported values,[14]

$$\chi = \frac{4\pi}{\epsilon} = \frac{4\pi}{C}(T - T_0), \qquad C = 3200^\circ\text{K}, \qquad T_0 = 49^\circ\text{C},$$

$$\xi = 72 \times 10^8 \frac{\text{cm}^4}{\text{coul}^2},$$

$\zeta = 4.1 \times 10^{20} \dfrac{\text{cm}^8}{\text{coul}^4}$ and the value for the spontaneous polarization, P_s, is $2.8 \times 10^{-6} \dfrac{\text{coul}}{\text{cm}^2}$ at 20° C. In the above values ϵ is the dielectric constant.

The change in energy of a virgin sample of TGS in going from the polar state at 20° C to the non-polar state at 49° C is given by Eq. (2a).

$$A = \frac{2\pi}{C}(20^\circ - 49^\circ)P_s^2 + \tfrac{1}{4}\left(72 \times 10^8 \frac{\text{cm}^4}{\text{coul}^2}\right)P_s^4 + \\ + \tfrac{1}{6}\left(4.1 \times 10^{20} \frac{\text{cm}^8}{\text{coul}^4}\right)P_s^6 + \qquad (2a)$$

Putting the terms of Eq. (2a) into the same units gives

$$A = -0.715\,\text{cal/g} + 0.18\,\text{cal/g} + 0.05\,\text{cal/g} = -0.49\,\text{cal/g}. \tag{2b}$$

This value is close to that obtained from the calorimeter measurements (average 0.73 cal/g). It is apparent from Eq. (2b) that it is justifiable to drop the P^6 term from the remainder of the discussion.

It is tempting to extend the thermodynamic treatment to irradiated TGS in the manner of the Okada[9] treatment for Rochelle salt. Following Okada, then, if a sample of TGS is irradiated with γ-rays, uncompensated charges are distributed homogeneously throughout the sample. The effect of these charges appears in the thermodynamic expansion for energy as a shift of the Curie point, ΔT_0, and an internal bias, E_b. Equation (1) then becomes

$$A = \frac{2\pi}{C}T - (T_0 - \Delta T_0)P^2 + \tfrac{1}{4}\xi P^4 - E_b P = A + \Delta A \tag{3}$$

Since $E \equiv \partial A/\partial P$ then

$$E = \frac{4\pi}{C}T - (T_0 - \Delta T_0)P + \xi P^3 - E_b. \tag{4}$$

Experimentally both ΔT_0 and E_b are linearly porportional to the radiation dose.

From the calorimeter measurement, ΔA, at a dose of 3×10^6 r, is 0.27 cal/g. If the measured values of ΔT_0 and E_b are used in Equation (3), however, ΔA is only about 0.07 cal/g. Even greater discrepancies exist if Equation (4) is solved for E_b and compared to the measured value of E_b. Equation (3) also predicts a linear dependence of ΔA on dose but this dependence is not found. It is concluded that such a simple thermodynamic treatment is insufficient for describing the irradiation effects of TGS.

The primary difficulty is applying thermodynamics to ferroelectrics lies in the fact that the theory is one for equilibrium states. In measurements of the specific heat anomaly equilibrium conditions are probably more nearly satisfied than in cases of electric measurements. A second difficulty is that it is difficult to account

for all contributions to a thermodynamic treatment. For instance, in the above discussion, no mention has been made of interaction between domains or defects produced by irradiation. Consequently, effects like the increase of coercive field and "a.c. annealing" remain unexplained for the present.

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