

Study of the Second-Order Ferroelectric Transition in Tri-Glycine Sulfate*

Abstract: Results of measurements of the dielectric constant, dielectric nonlinearity and spontaneous polarization of tri-glycine sulfate are given. These data demonstrate clearly that this material exhibits a second-order ferroelectric transition. The properties discussed are described in terms of the usual expansion of the free energy in even powers of the polarization

$$F(P, T) = F(O, T) + A(T - T_0)P^2 + BP^4 + CP^6,$$

where A , T_0 , B and C are constants and T and P are the temperature and polarization, respectively. From the various data taken it is found that $A = 1.96 \times 10^{-3} (\text{°C})^{-1}$, $T_0 = 49.8^\circ\text{C}$, $B = 2.0 \times 10^{-10} (\text{esu/cm}^2)^{-2}$ and $C = 8.4 \times 10^{-19} (\text{esu/cm}^2)^{-4}$. From these results the nonlinearity of the dielectric constant above the Curie point is calculated at various temperatures.

Introduction

The purpose of this work is to report the detailed behavior of one of the more recently reported ferroelectrics, tri-glycine sulfate.¹ There is considerable technological interest in this material since it is grown quite easily from water solution and has some rather favorable ferroelectric properties.

The scope of this work includes investigations of the dielectric constant, spontaneous polarization and nonlinear dielectric behavior. All of these can be correlated by the type of thermodynamic analysis proposed by Devonshire.² The free energy of a stress-free crystal is expanded as a function of polarization and temperature about the point $P=0$,

$$F(P, T) = F(O, T) + A(T - T_0)P^2 + BP^4 + CP^6 + \dots \quad (1)$$

in which the polarization-dependent part appears as an even function of P . The coefficient of P^2 has taken account of the experimentally observed Curie-Weiss behavior above the temperature T_0 . A , B , and C are assumed to be constants, while $F(O, T)$ constitutes the polarization-independent part of the free energy.

From Eq. (1) and the thermodynamic relations

$$\frac{\partial F}{\partial P} = E \quad (2a)$$

$$\frac{\partial^2 F}{\partial P^2} = \frac{\partial E}{\partial P} = \frac{4\pi}{\epsilon - 1} \doteq \frac{4\pi}{\epsilon} \quad (2b)$$

it is possible to correlate all of the measurements reported here. In fact, the validity of this phenomenological treatment is tested by the ability to correlate all of these results by one set of constants A , B , C , and T_0 .

Such analysis has been applied with great success to a variety of observations³ in BaTiO_3 and KNbO_3 . In these perovskite ferroelectrics the coefficient B in Eq. (1) has been found to be negative. As a consequence, first-order ferroelectric transitions occur at a temperature T_c related to the other coefficients by

$$A(T_c - T_0) = B^2/4C.$$

In the compound discussed in this paper (which for convenience will be called T.G.S.) B has been found to be positive. A second-order ferroelectric transition occurs at the temperature T_0 . The relation given by Eq. (2b) indicates that in the paraelectric state ($T > T_0$), where the spontaneous polarization (denoted from now on by P_s) is zero, the dielectric constant is given by:

$$\epsilon - 1 \simeq \epsilon = (2\pi/A)(T - T_0)^{-1}. \quad (3)$$

Eq. (3) predicts Curie-Weiss behavior with a Curie constant given by $(2\pi/A)$. Furthermore, it is apparent from Eq. (3) that the dielectric constant tends to infinity as T approaches T_0 . The corresponding actual physical behavior is essentially a saturation of the susceptibility at relatively low electric fields, namely, high nonlinearity in the dielectric constant. If bridge measurements are made with "vanishingly" small fields, large values of ϵ are observed near T_0 , the actual peak being determined by

*This paper was presented at the 1957 March meeting of the American Physical Society, Philadelphia, Pa.

the quality of the electrodes and of the crystal. Values of ϵ greater than 10^5 have been recorded for T.G.S.

In materials exhibiting first-order transitions, the peak dielectric constant is limited by the fact that a transition to the ferroelectric state occurs before the temperature T_0 is reached. In the ferroelectric state, P is no longer zero and the terms in P essentially lead to a spontaneous saturation of the susceptibility.

The dielectric constant

Figure 1 shows a typical plot of the dielectric constant as a function of temperature taken on an XY recorder.⁴ In Fig. 2 are given the results of measurements of the reciprocal dielectric constant as a function of temperature for a number of samples. From Eq. (3), the slope of the line determined by the data above the Curie point yields a value of A while the intercept on the abscissa is T_0 . From these data $A = 1.96 \times 10^{-3} (^{\circ}\text{C})^{-1}$ and $T_0 = 49.8^{\circ}\text{C}$.

The value T_0 and the transition temperature coincide, in contrast with the first-order case for which the transition temperature is higher than T_0 . (In the case of BaTiO_3 , T_0 is 11°C below the transition temperature while for KNbO_3 it is 58°C below.) It is found also for T.G.S. that there is no thermal hysteresis in the transition temperature on heating and cooling, again in contrast with first-order materials which do exhibit definite thermal hysteresis.

To understand the behavior of ϵ below the Curie point it must be realized that at the actual ac measuring frequency (10 kc) the measurement is adiabatic rather than isothermal. The relation derived from Eqs. (1) and (2b) must be modified as follows:⁵

$$\left(\frac{\partial E}{\partial P}\right)_s = \frac{4\pi}{\epsilon_s - 1} \left(\frac{\partial E}{\partial P}\right)_T + T \left(\frac{\partial E}{\partial T}\right)_P / C_P \rho \quad (4)$$

where ϵ_s is the dielectric constant at constant entropy, ρ is the mass/cm³ and C_P is the heat capacity per gram at constant polarization. From Eqs. (1) and (4)

$$\frac{4\pi}{\epsilon_s - 1} = 2A(T - T_0) + 12BP_s^2 + 30CP_s^4 + \frac{4A^2T}{C_P \rho} P_s^2. \quad (5)$$

It can be shown that

$$P_s^2 = - \frac{A(T - T_0)}{2B} \quad (6)$$

in the region just below the temperature T_0 . In this region of small values of $(T - T_0)$

$$\frac{4}{\epsilon_s - 1} = -4A(T - T_0) \left[1 + \frac{A^2T}{2C_P \rho B} \right]. \quad (7)$$

The adiabatic correction term $(A^2T/2C_P \rho B)$ turns out to be negligible in the case of BaTiO_3 and KNbO_3 . From the published values of C_P , ρ and the value of B given in the following section for T.G.S., this represents a

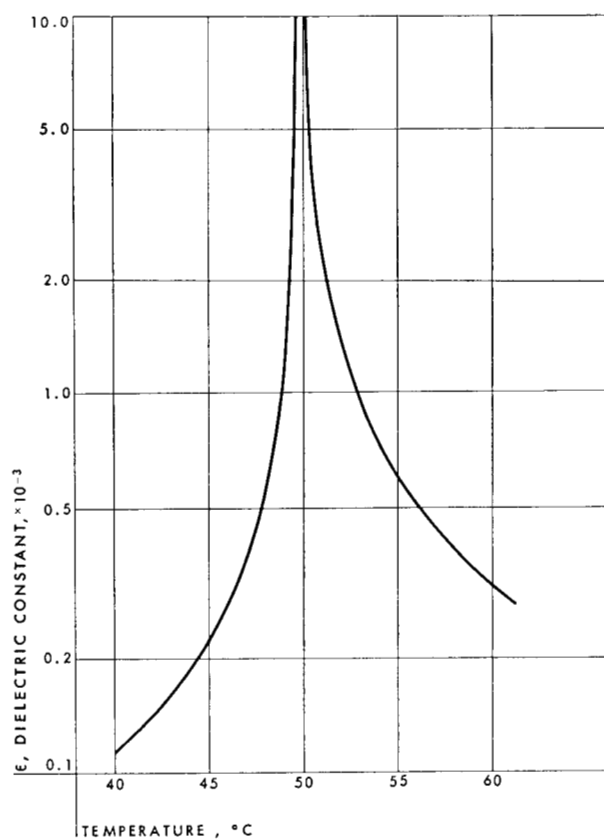
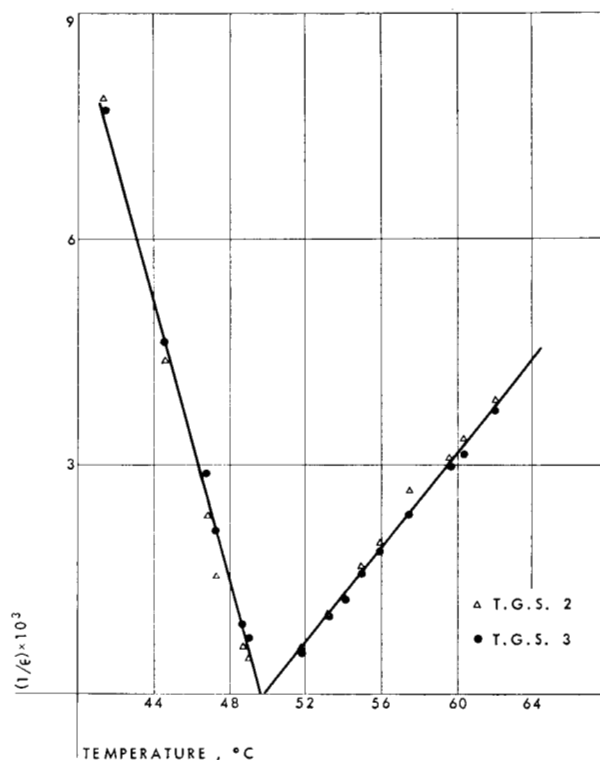


Figure 1 Dielectric constant (ϵ) vs temperature. Measurements are made at 25 kc.

Figure 2 $1/\epsilon$ vs temperature at 25 kc.



correction of about 20%. If this correction were negligible the ratio

$$\frac{\left[\frac{d(1/\epsilon)}{dT} \right]_{T < T_0}}{\left[\frac{d(1/\epsilon)}{dT} \right]_{T > T_0}} = -2. \quad (8)$$

The expected experimental value including the adiabatic correction is 2.4. From Fig. 2 the ratio is 3.0. Measurements on two other crystals yield values of 2.3 and 2.7. The scatter and residual discrepancy may be explained by the fact that the crystals may have 180° walls below the Curie point, associated with which will be domain clamping.⁸

Measurements of ϵ along the a and c directions (the monoclinic b axis is the ferroelectric direction) show normal dielectric constants (~ 10). This fact is important in situations where fringing field effects are to be considered.

Spontaneous polarization

Figure 3 shows the spontaneous polarization (P_s) and coercive field (E_c) as a function of the temperature. The break in E_c at about 38°C is real, having been observed

by other workers.⁹ The origin of this anomaly is not understood.

From the thermodynamic relation Eq. (2a) and Eq. (1), for a crystal with the electric field equal to zero,

$$P_s^2 = \frac{A(T_0 - T)}{2B} - \frac{3}{8} \frac{A^2 C}{B^3} (T_0 - T)^2 \quad (9)$$

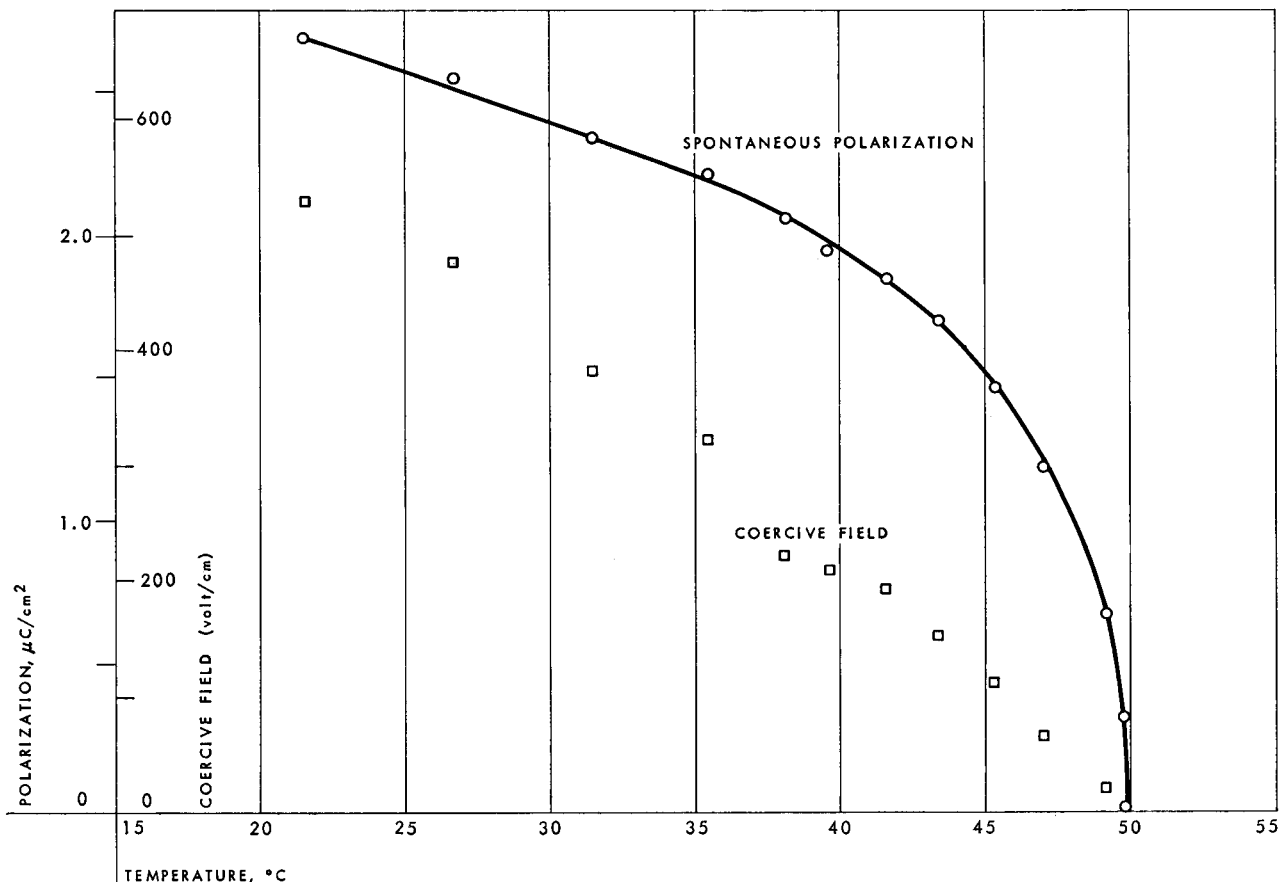
in the region of T where the second term is small compared with the first. By a least squares fitting of the P^2 vs. $(T - T_0)$ data in the vicinity of T_0 , B and C can be found. The results are:

$$B = 2.0 \times 10^{-10} (\text{esu/cm}^2)^{-2}$$

$$C = 8.4 \times 10^{-19} (\text{esu/cm}^2)^{-4}.$$

It is worth noting that validity of the power series expansion for the free energy as judged by convergence is more satisfactory in the case of T.G.S. than in BaTiO₃ or KNbO₃. For T.G.S., if we evaluate the P^2 , P^4 and P^6 terms at 40°C where $P_s \sim 2 \mu\text{C/cm}^2$, it is found that they contribute $7.3 \times 10^5 \text{ erg/cm}^3$, $2.6 \times 10^5 \text{ erg/cm}^3$ and $0.4 \times 10^5 \text{ erg/cm}^3$, respectively. In the case of the last two materials it is found actually as a direct consequence of the theory that the P^2 and P^6 terms yield equal contributions, while the P^4 term is twice as large as either at the transition temperature.⁴

Figure 3 Spontaneous polarization and coercive field for sine wave driving fields at 200 cps.



Nonlinear dielectric constant

Using a method essentially identical with that described by Drougard et al,¹⁰ the value of B was measured directly above the Curie point. The technique involves applying a low-frequency (200 cps in this case), high-amplitude biasing field while a crystal is in a bridge in which the measuring signal is of low amplitude and high frequency (50 kc in this case). The nonlinearity in ϵ leads to an unbalance of the bridge output with application of the biasing field. When the unbalance voltage is applied to the vertical deflection plates of an oscilloscope and the induced polarization to the horizontal plates, it is possible to observe the relation between ϵ and P^2 .

Since the measurement is essentially adiabatic, as discussed by Drougard et al,¹⁰ the observed shift in ϵ must be analyzed from Eq. (6) of Reference 10:

$$4\pi/\epsilon = 2A(T-T_0) + 12 \left[B + \frac{TA^2}{2C_P\rho} \right] P^2. \quad (10)$$

The value P now is the polarization induced by the low-frequency field applied in the paraelectric state ($T > T_0$). The second term in the coefficient of P^2 constitutes an adiabatic correction similar to that discussed in the section entitled "Spontaneous Polarization."

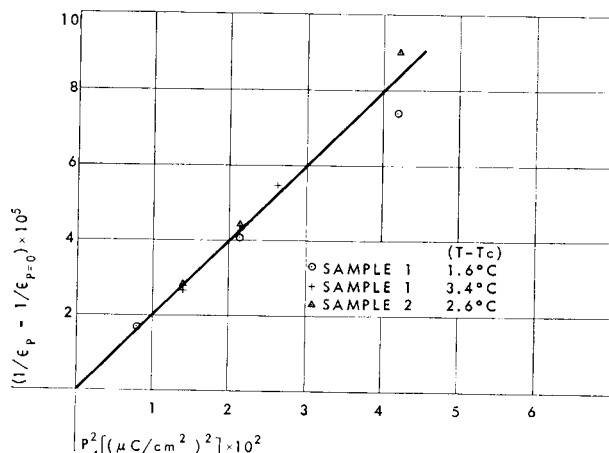
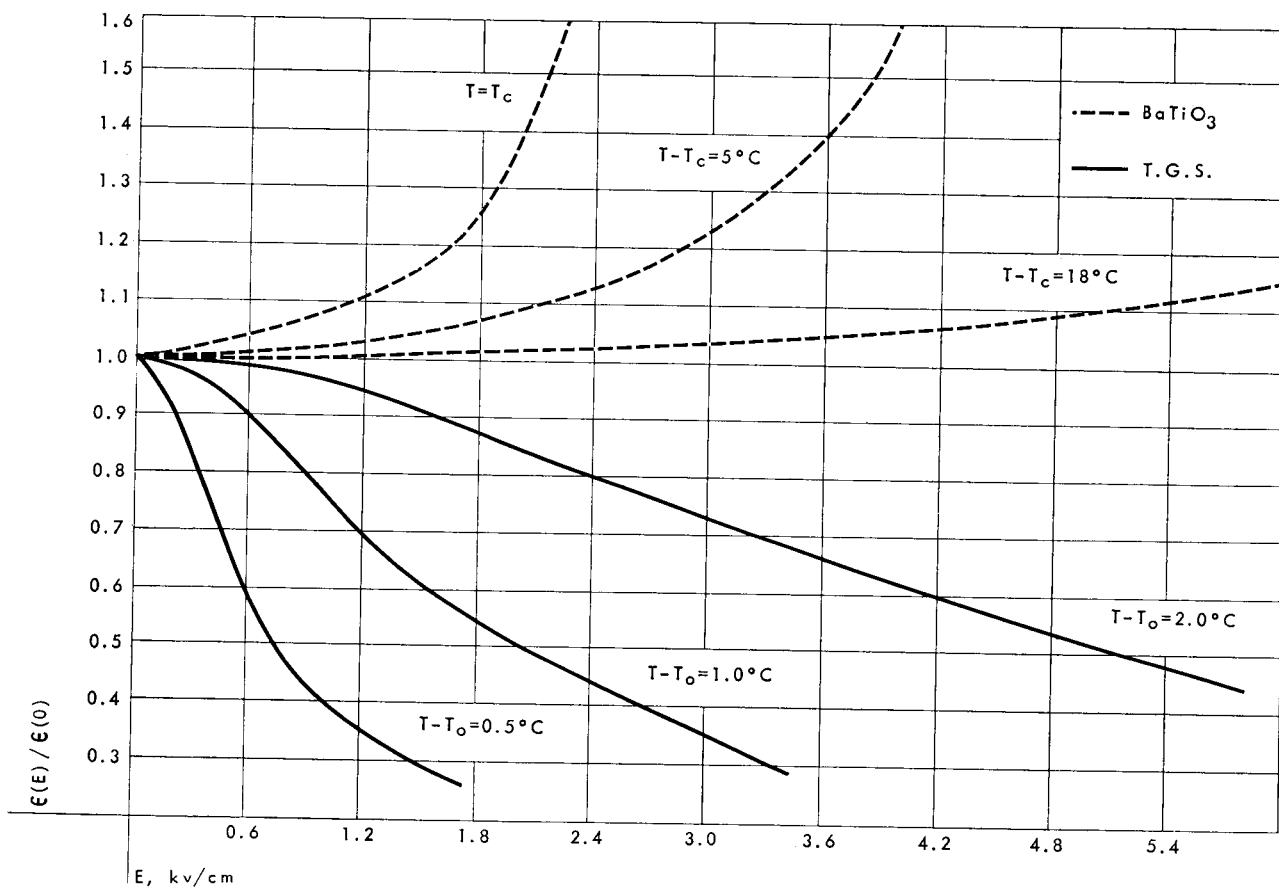


Figure 4 $(1/\epsilon)_P - (1/\epsilon)_{P=0}$ vs P^2 .
Biasing field is 200 cps sine wave,
measuring field 50 kc.

Figure 4 shows $(1/\epsilon)_P - (1/\epsilon)_{P=0}$ for various values of P^2 and temperature for a number of crystals. Here $(1/\epsilon)_{P=0}$ is, of course, equal to $(A/2\pi)(T-T_0)$. From the slope of the best line through the data:

Figure 5 $\epsilon(E)/\epsilon(0)$ for various biasing fields and temperature for BaTiO_3 and T.G.S.



$$B + \frac{TA^2}{2C_P P} = 2.3 \times 10^{-10} \text{ cgs.}$$

Since the adiabatic correction is 0.38×10^{-10} cgs, we have $B = 1.92 \times 10^{-10}$ cgs. This is in excellent agreement with the results obtained from the spontaneous polarization data.

From Eqs. (2a) and (10) it is possible to calculate E and $4\pi/\epsilon$ for a given value of P . From these results it is possible to correlate ϵ with E . Figure 5 shows $\epsilon(E)/\epsilon(E=0)$ for both BaTiO_3 and T.G.S. It is understood here that ϵ represents the small-signal or incremental dielectric constant as defined in Eq. (2b). E is the dc bias field. If the bias were to be applied adiabatically the curve for T.G.S. would show a somewhat smaller non-linearity, but the BaTiO_3 data would be unaffected.

In Figs. 6a and 6b are shown the effect on capacitance of applying a dc-biasing electric field to a T.G.S. condenser made by evaporating gold on opposite faces of a plate cut so that E is parallel to the ferroelectric axis. The crosses show theoretical values, while the solid lines are taken from an XY recorder in which the X axis shows bias voltage and Y axis the capacitance.

Two qualitative differences are observed between the

first-order material (BaTiO_3) and the second-order material (T.G.S.). In the region just above T_c the former shows an increase of ϵ with field, while in the latter ϵ decreases. Secondly, BaTiO_3 exhibits double-loop behavior in the region $T_c < T < (T_c + 18^\circ\text{C})$. If excessive biasing fields are applied the E vs P characteristic is not single valued. T.G.S. simply saturates, with no complications. Both of these effects are related to the sign of B .

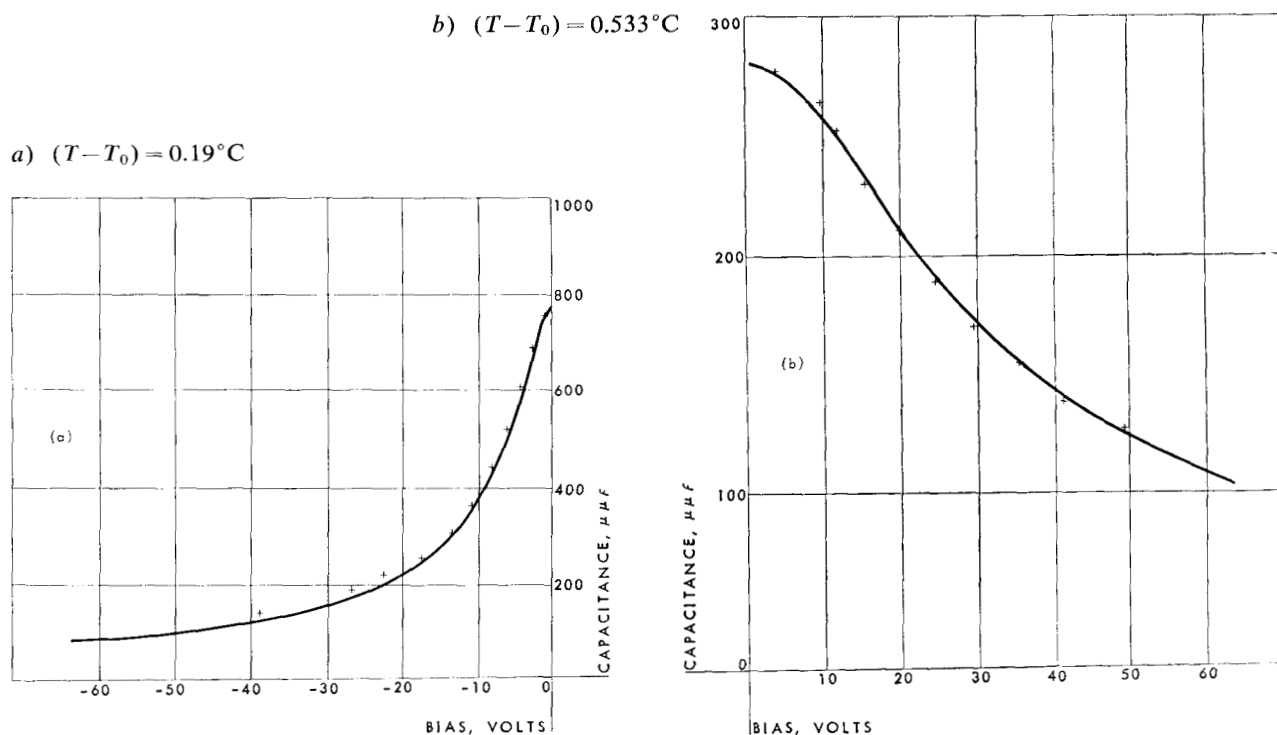
Conclusions

It has been demonstrated that tri-glycine sulfate exhibits a second-order ferroelectric transition, which is analyzed in detail according to the Devonshire phenomenological theory. The applicability of this treatment is demonstrated by:

1. Comparison of the dielectric constant above and below the Curie point.
2. The consistency of B determined from nonlinear dielectric data above the Curie point and the variation of the spontaneous polarization with temperature below the Curie point.

For purposes of classification, tri-glycine sulfate falls in the undefined category of ferroelectrics which includes

Figure 6 C vs bias volts. T.G.S. crystal is 0.056 cm thick. Crosses are theoretically calculated points. Solid line shows measurement taken on XY recorder.



KH_2AsO_4 , KH_2PO_4 and rochelle salt as judged by the value of A . All of these have $A \sim 10^{-3} (\text{°C})^{-1}$. The perovskite ferroelectrics, on the other hand, have A values of order $10^{-5} (\text{°C})^{-1}$. In the latter case (BaTiO_3 for example) the observed free energy is predictable on the basis of a theory proposed by Devonshire² and Slater¹¹ from which the order of magnitude of A can be predicted. The situation has not been so clearly defined for the former group of materials.

It appears that materials like tri-glycine sulfate will be more useful than first-order ferroelectrics as single-crystal nonlinear dielectrics above the Curie point because of the high nonlinearity that is attainable without the undesirable instabilities associated with the double loops.

Acknowledgments

I would like to express appreciation to Bell Telephone Laboratories and J. P. Remeika and B. T. Matthias in particular for contributing the crystals of tri-glycine sulfate on which some of the earlier measurements were made. J. E. Scardefield and M. M. Whitehill of this laboratory and K. Asai of the IBM Watson Research Laboratory prepared the crystals for these measurements.

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Received March 4, 1958