SET OF EXPERIMENTAL CRITICAL EXPONENTS FOR FERROELECTRIC TRIGLYCINE SULFATE

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A series of curves of P vs E at various temperatures close to the transition temperature of triglycine sulfate have been used for determining the behavior of P, $(\partial P/\partial E)_{T \simeq T_c}$, and $(\partial P/\partial T)_{E=0}$ with respect to field and temperature in the critical region. Log-log plots of the polarization and its derivatives versus E and T allow the direct experimental determination of six critical exponents. All of these experimental values are consistent with predictions of the mean-field theory.

Observations of hysteresis loops (P vs E) from ferroelectrics are a very good means of obtaining information about the critical behavior of these substances. A series of hysteresis loops at various temperatures near the transition temperature can provide information not only on the behavior of spontaneous polarization with temperature but also on polarization with field and, if the resolution is good enough, on the successive derivatives of polarization with respect to field and temperature. A set of critical exponenets obtained in this way, which permits a full characterization of the behavior of the second-order transition ferroelectric triglycine sulfate (TGS), is reported in this Letter.

The sample preparation ("gold leaf" electrodes) and experimental procedure were described in detail elsewhere.[1] Pictures of the hysteresis loops were collected from the 'scope screen by means of a photographic camera. The pictures were enlarged to a size about six times the original one, and the hysteresis loops at different temperatures were reproduced on a single graph sheet taking care to correct for drifts of the origin of the loop from picture to picture. The readings of polarization (P) as a function of field (E) and temperature (T) were taken from both sides of the highly symmetric hysteresis loop and then averaged. The amplitude of the field applied to the sample was kept fixed for all measurements at about 190 V/cm. It may be noted that the curve of P vs E is somewhat dependent on field amplitude, showing slightly enhanced values of P for all values along the E axis as the field amplitude is increased.

Figures 1(a) and 1(b) show log-log plots of P vs E, at a temperature very close to T_c ($t = T_c - T = 0.042°C$) and of P_s vs T at $E = 0$. Figures 2(a) and 2(b) show the behavior of $\Delta P/\Delta E$ at $t = 0.042°C$ and $\Delta P/\Delta T$ at $E = 0$, as a function of E and T. For Fig. 2(a) the increment used to compute $\Delta P/\Delta E$ was $\Delta E = 7.05$ V/cm, and for $\Delta P/\Delta T$, ΔT was 0.13°C. A reduced field scale is shown in which the actual electric field value is divided by the ferroelectric local field at saturation polarization, $\beta N\mu = 3.9 \times 10^5$ V/cm. For Fig. 2(b), the increment used to obtain $\Delta P/\Delta E$ was $\Delta E = 1.41$ V/cm, and for $\Delta P/\Delta T$, ΔT was again

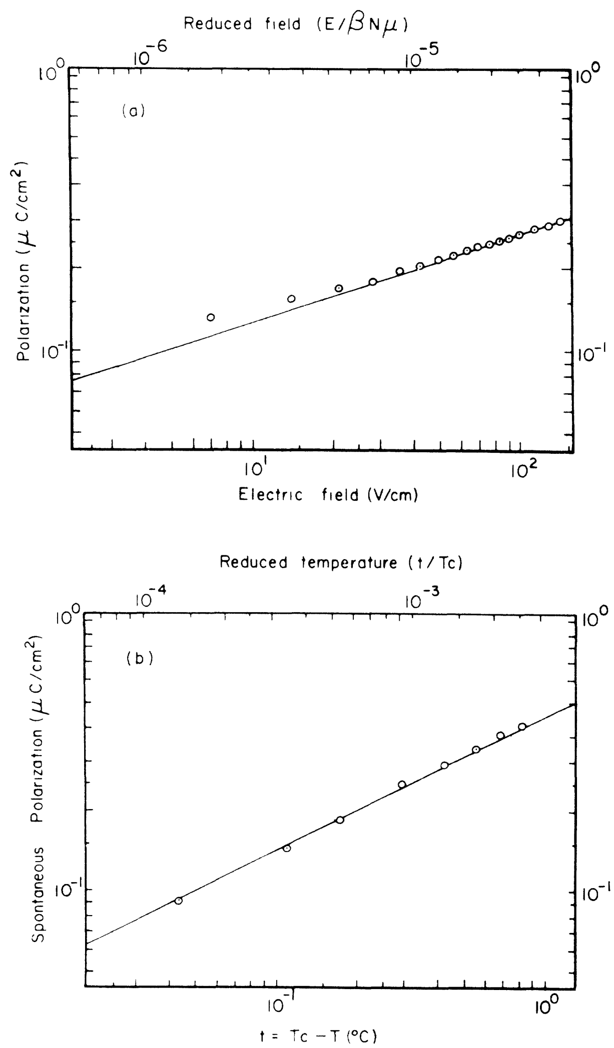

FIG. 1. Log-log plots of (a) polarization versus field at $t = T_c - T = 0.042°C$ and (b) spontaneous polarization versus temperature at $E = 0$.

0.13°C. The reduced temperature scale t/T_C, with $T_C = 322°K$, is also shown. It should be remarked that for graphs of P and derivatives of P as a function of field, one can represent as many points as one wishes, since they are taken from a continuous curve. On the other hand, similar graphs as a function of temperature have a limited number of points since the number of photographs at different temperatures was limited.

The critical exponents for the whole set of derivatives of the ferroelectric free energy (F) may be labeled in the following way:

$$F(E,T)_{T=0} \sim E^{\gamma_1}; \quad F(E,T)_{E=0} \sim t^{\gamma_2}; \tag{1}$$

$$(\partial F/\partial E)_{T=0} \sim E^{\gamma_3}; \quad (\partial F/\partial E)_{E=0} \sim t^{\gamma_4}; \quad (\partial F/\partial T)_{T=0} \sim E^{\gamma_5}; \quad (\partial F/\partial T)_{E=0} \sim t^{\gamma_6};$$

$$(\partial^2 F/\partial E^2)_{T=0} \sim E^{\gamma_7}; \quad (\partial^2 F/\partial E^2)_{E=0} \sim t^{\gamma_8}; \quad (\partial^2 F/\partial E\partial T)_{T=0} \sim E^{\gamma_9}; \quad (\partial^2 F/\partial E\partial T) \sim t^{\gamma_{10}}; \tag{2}$$

$$(\partial^2 F/\partial^2 T^2)_{T=0} \sim E^{\gamma_{11}}; \quad (\partial^2 F/\partial T^2)_{E=0} \sim t^{\gamma_{12}}; \cdots. \tag{3}$$

Recalling that $P = (\partial F/\partial E)$, the data shown in Figs. 1(a), 1(b), 2(a), and 2(b) enable us to compute the critical exponents $\gamma_3, \gamma_4, \gamma_7, \gamma_8, \gamma_9, \gamma_{10}$. This can be done directly by measuring the slope on the log-log plots. The results are

$$\gamma_3 = \frac{1}{\delta} = 0.32 \pm 0.02 \sim \tfrac{1}{3}; \quad \gamma_4 = \beta = 0.50 \pm 0.03 \sim \tfrac{1}{2}; \quad \gamma_7 = -0.66 \pm 0.05 \sim -\tfrac{2}{3}; \quad \gamma_8 = \gamma' = -0.95 \pm 0.10 \sim -1;$$

$$\gamma_9 = -0.33 \pm 0.05 \sim -\tfrac{1}{3}; \quad \gamma_{10} = -0.46 \pm 0.10 \sim -\tfrac{1}{2}.$$

The estimated relative error in readings of polarization from the enhanced plot of P vs E curves was 0.5 to 2%. However, some of the plots of the derivatives of P contained accumulative errors. Deviations from the straight line near the origin in the log-log plots may be attributed to two sources. One is that, in the region close to $E = 0$, the curvature of the P vs E curves is large and the ratio of increments is considerably lower than the true derivative. As the departure from $E = 0$ increases, the curvature decreases and the ratio of increments becomes truly representative of the derivative. This consideration applies especially in the case of Fig. 2(b), where $(\partial P/\partial T)_{E=0}$ and $(\partial P/\partial E)_{E=0}$ vs T are represented. The other source is the fact that the data giving P and its derivatives versus E have been taken close to T_C, but at a finite $t = T_C - T = 0.42°C$, and so they include some residual polarization which should not be there if the temperature had been T_C ($t = 0$). This is the case of Fig. 1(a), where the actual values of P close to $E = 0$ are higher than what should be expected for $t = 0$. In the case of Fig. 2(a), one has the two sources of deviations competing with each other. However, in all cases there is a sufficient portion of the data showing unambiguously a straight-line behavior, with the possible exception of $(\partial P/\partial E)_{E=0}$ vs T in Fig. 2(b). Fortunately in this case we already have direct evidence,[1] from dielectric-constant measurements, that the corresponding critical exponent is $\gamma_6 = -1.00 \pm 0.05$, which confirms the result drawn from Fig. 2(b) using only the last few points. A possible objection against the validity of dielectric-constant measurements to show the true "monodomain" crystal behavior may be answered by noting that in ferroelectrics[2] the thickness of the transition layer at the domain wall is very small (of the order of one lattice constant), indicating that a "polydomain" single crystal may well be looked upon as consisting of two sets of "monodomain" crystals.

All the results reported here are in excellent agreement with the mean-field theory (which predicts $\gamma_{2n-1}/\gamma_{2n} = \frac{2}{3}$, $n = 1, 2, 3, \cdots$). To complete the picture, data on the dependence of critical behavior of the specific heat on field and temperature would be of interest. While we lack detailed information on the specific-heat behavior, available data from Strukov,[3] using a single crystal, and from Tello,[4] using powder, also seem to indicate agreement with the mean-field theory. Figure 3 shows a log-log plot of the ferroelectric specific heat versus temperature from their results. It is seen in this plot that as $t = T - T_C \to 0$, the ferroelectric specific heat $C_E = (\partial^2 F/\partial T^2)_{E=0} \to$ constant which would imply $\gamma^{12} = \alpha' = 0$.

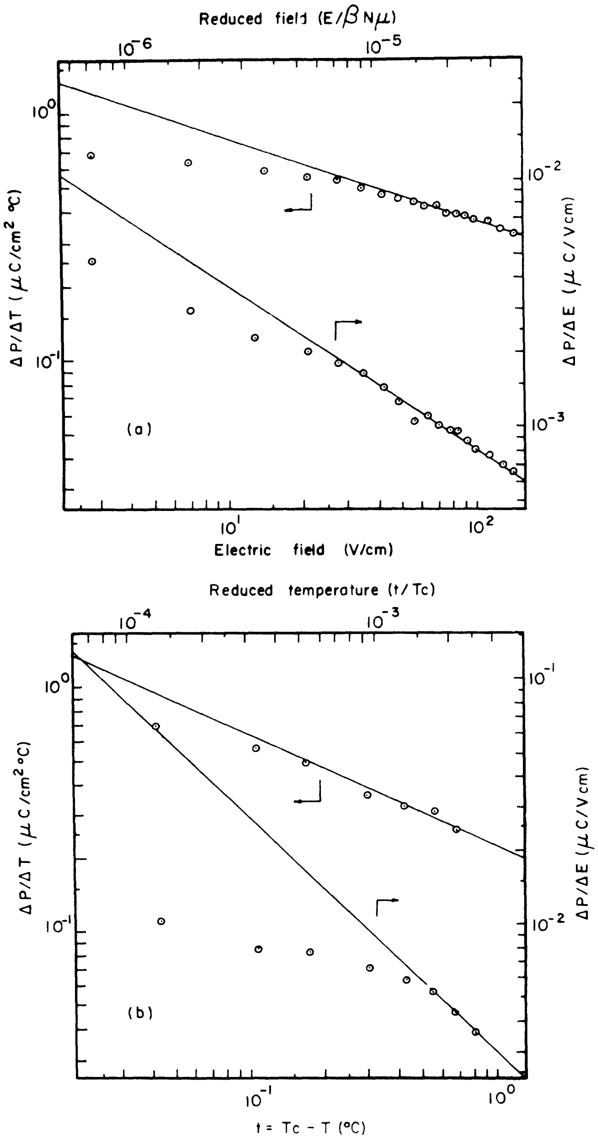

FIG. 2. Log-log plots of (a) derivatives of polarization (with respect to temperature and field) versus field and (b) derivatives of polarization (with respect to temperature and field) versus temperature.

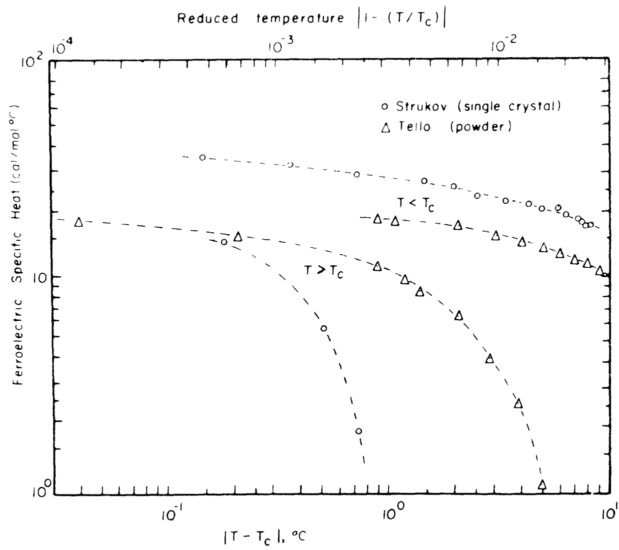

FIG. 3. Log-log plot of ferroelectric specific heat versus temperature.

It is interesting to note that the anomalies in the linear and volume expansion coefficients that accompany the transition seem to have no effect in modifying the mean-field pattern of the critical behavior. This supports the idea that they are a consequence and not a cause of the dielectric behavior.

Several remarks may be made in connection with the present work: (a) The good agreement between experimental data and mean-field theory strongly suggests a reconsideration of the currently somewhat disregarded dipolar theory of ferroelectrics as a basis for developing a successful theory. (b) The knowledge of a full set of critical exponents, as those reported here, may enable one to establish additional "scaling laws," and in the end, to define the fundamental parameter, or parameters, from which all critical exponents can be deduced. (c) The method of analysis described here may be applicable to the case of ferromagnetic systems starting with a series of M vs H curves at different temperatures close to the Curie point. Modifications of this method may be applied to antiferromagnets (or antiferroelectrics) by using χ_E vs T (or ϵ vs T) at different H (or E), C_H vs T (or C_E vs T) at different H (or E), etc.

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[2]F. Jona and G. Shirane, Ferroelectric Crystals (Pergamon Press, New York, 1962).

[3]B. A. Strukov, Fiz. Tverd. Tela 6, 2862 (1964) [translation: Soviet Phys.-Solid State 6, 2278 (1965)].

[4]M. Tello, private communication.