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Critical Behavior of Ferroelectric Triglycine Sulfate

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The ferroelectric behavior of triglycine sulfate, which can be considered the best example of a nearly ideal second-order-transition ferroelectric, has been analyzed. Accurate measurements of the temperature dependence of spontaneous polarization and dielectric constant in the vicinity of the phase transition from the ferroelectric to the nonpolar state were performed, yielding the following results: $P_s=\text{const}\times(\Delta T)^{\beta}$ with $\beta=0.51\pm0.05$ and $1/\epsilon=\text{const}\times(\Delta T)^{\gamma}$ with $\gamma=1.00\pm0.05$, both above and below, but close to, the critical temperature T_c. These results are in good agreement with predictions of the thermodynamic theory for ferroelectric crystals.

I. INTRODUCTION

RECENT highly accurate experimental data[1,2] and theoretical developments[3,4] concerning the critical behavior of ferro- and antiferromagnetic phase transition suggest the extension of similar investigations to the case of ferroelectric transitions. Among typical order-disorder ferroelectrics, triglycine sulfate (TGS) appears to be a good choice for examination of behavior near the critical temperature because of the "regularity" of its behavior in comparison with other second-order-transition ferroelectrics.

Previous experimental work[5–7] on the ferroelectric parameters of TGS were not primarily concerned with the critical behavior. On the other hand recent and very accurate dielectric-constant measurements by Sekido and Mitsui[8] were directed toward the study of the peak value of this physical property rather than its behavior in the critical region.

The present investigation gives an account of hysteresis loop and capacitance measurements on single crystals of TGS taken in the vicinity of the critical temperature, which enables us to characterize the cooperative order-disorder transition through the temperature variation of spontaneous polarization and susceptibility. Recently Craig[9] has carried out the dielectric measurements of TGS, and also of Rochelle salt and potassium dihydrogen phosphate, near the critical point.

II. EXPERIMENTAL

The samples were single-crystal plates cleaved perpendicular to the ferroelectric axis from a very perfect, large crystal grown at the IBM Research Center, New York. We are grateful to Triebwasser for making the samples available to us. These plates were ground with emery paper and the surfaces further polished on a slightly wet cloth to obtain perfect rectangular shapes. The area of the samples was about 0.45 cm^2 and the thickness about 0.80 mm. The electrodes were made of very thin good foil attached directly to the main surfaces of the crystal, the same technique as was used previously by Okada[10] for Rochelle salt crystals. Both surfaces perpendicular to c axis were completely covered. This method avoided possible strains in the surface of the sample, which might have occurred if other conventional methods, such as silver paint or noble-metal evaporation, had been used. The quality of the samples was tested, after cycling the sample temperature several times through T_c, by means of observations of the hysteresis loop shape and the peak value of the dielectric constant. The effects on the dielectric constant below and in the vicinity of T_c of a small variable dc field superimposed on the small ac signal were also examined. For a given temperature, the value of dielectric constant decreased quite steadily and by the same amount for dc fields of equal size and opposite polarity. This equal decrease means that no spontaneous internal bias caused by impurities was present in the crystal or, rather, that it was undetectably small under our experimental conditions.

The sample holder, in which care was taken to avoid excessive mechanical pressure on the sample surfaces from the electrical contacts, was introduced in a thick-walled aluminum container. To avoid disturbances from moisture deposited on the crystal surfaces, a small amount of a desiccant (SiO$_2$) was placed inside the container. For temperature control, a large Dewar full of water, with the top covered by thermally insulating material, was used. A thermocouple, very near the sample, and with its cold junction inside an ice bath, measured the sample temperature. Regulated heat input from an adjustable-voltage electrical heater provided the desired temperature in the continuously stirred bath. After every heat input (heating rate 0.10°C/min.) the system was allowed to reach thermal equilibrium. For very accurate measurements in the immediate

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* Operated by the University of Puerto Rico for the U. S. Atomic Energy Commission.

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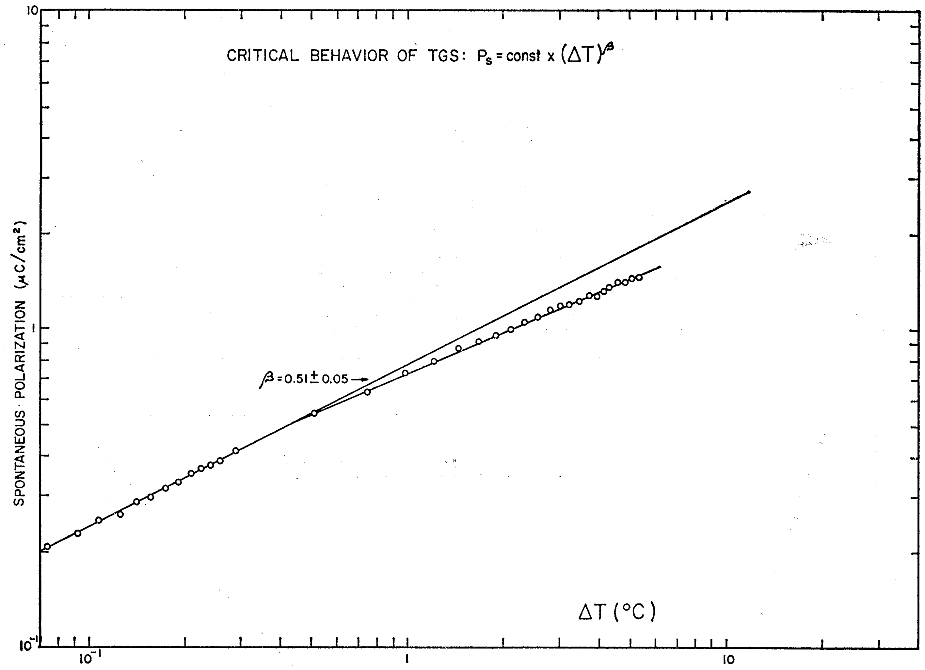

FIG. 1. Log-log plot of spontaneous polarization versus temperature for ferroelectric triglycine sulfate in the vicinity of the critical temperature.

vicinity of the transition temperature, the system was heated well above T_c and allowed to spontaneously cool through the transition. The cooling rate was about 0.0085°C/min and, from thermocouple readings every 10 min. was found to be nearly linear with time. The temperature change between capacitance readings could be accurately determined from the time between measurements.

For the hysteresis-loop measurements, a Sawyer-Tower circuit,[11] with allowance for phase compensation, and a Diamant-Drenck-Pepinsky[12] circuit were used in a preliminary stage. Observations made with the former showed better reproducibility, and subsequently all data collected thereafter were obtained using the Sawyer-Tower circuit. The 60-cps hysteresis loops were displayed on the screen of a Tectronix 536 oscilloscope.

Capacitance measurements were performed by direct reading from a 716-C General Radio bridge and a 650-PI General Radio bridge. The frequency of the small a.c. applied signal (~0.5 V/cm) was 1 kc/sec. As detectors we used simultaneously earphones and a high-amplification oscilloscope, which permitted us to follow the effect of nonlinearity on the output sine wave from the bridge when passing through the critical temperature.

III. SPONTANEOUS POLARIZATION

The results for spontaneous polarization are given in Fig. 1. The amplitude of the applied field was 400 V/cm and the frequency 60 cps. The estimated error for these measurements, using the appropriate amplification in the oscilloscope, is below 5%. Spontaneous polarization versus temperature is well described by $P_s = \text{const}\times(\Delta T)^\beta$, with $\beta = 0.51\pm0.05$ in the vicinity of T_c. It should be mentioned that the usual definition of spontaneous polarization P_s had to be revised for hysteresis-loop observations very near T_c. Currently, P_s is defined as the value obtained by extrapolating the saturation branch of the hysteresis loop to zero field. This definition would imply $P_s \neq 0$ even above T_c, due to the nonlinearity of the P-E curve. We decided to take the actual ordinate for zero field in the hysteresis loop as the true P_s, which at lower temperatures coincided with the usual definition (owing to the rectangularity of the loops).

The data given in Fig. 1 permit the calculation of the coefficients in the free-energy expansion by using (see for example, Jona and Shirane[13]) the formula

$$P_s^2 = -\frac{1}{\xi}\frac{4\pi}{C}(T_c - T) - \frac{\zeta}{\xi^3}\left[\frac{4\pi}{C}(T_c - T)\right]^2, \qquad (1)$$

where C is the Curie constant. The results are $\xi = (6.9\pm0.7)\times10^{-10}$ esu and $\zeta = (8.2\pm2.0)\times10^{-18}$ esu. The results can be compared with those of Triebwasser,[6] $\xi = 8.0\times10^{-10}$ esu and $\zeta = 5.0\times10^{-18}$ esu, determined using a much wider temperature interval which included only a few points in the critical region.

The behavior of the coercive field E_c in the critical region was examined simultaneously, indicating a temperature dependence given by $E_c = \text{const}\times(\Delta T)^\delta$ with

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$\delta = 0.79 \pm 0.10$, which, as is expected, deviates strongly from the value predicted by the thermodynamic theory, $\delta = \frac{3}{2}$ at the vicinity of T_c.

IV. DIELECTRIC CONSTANT

The results of dielectric constant measurements are given in Figs. 2(a)–(b). The accuracy in capacitance measurements was always better than 1%. The Curie-Weiss law is perfectly obeyed in the critical region: $1/\epsilon = \mathrm{const} \times (\Delta T)^{\gamma}$, with $\gamma = 1.0 \pm 0.01$. This behavior is followed both above and below $T_c = 49.42 \pm 0.05$°C, in agreement with the requirements of the phenomenological thermodynamic theory. It may be pointed out that the extrapolation of the paraelectric and ferroelectric branches meet each other on the base line ($1/\epsilon = 0$) indicating that the real trend of the dielectric constant is toward infinity at T_c. Among the possible factors reducing the peak value at the transition temperature one could mention edge effects at the sample capacitor, the presence of small internal biases and thermal gradients, and also clamping effects from the electrical contacts to the electrodes. From Fig. 2(b) the ratio of Curie constants below and above the transition can be determined: $C^{-}/C^{+} = 2.42$, in excellent

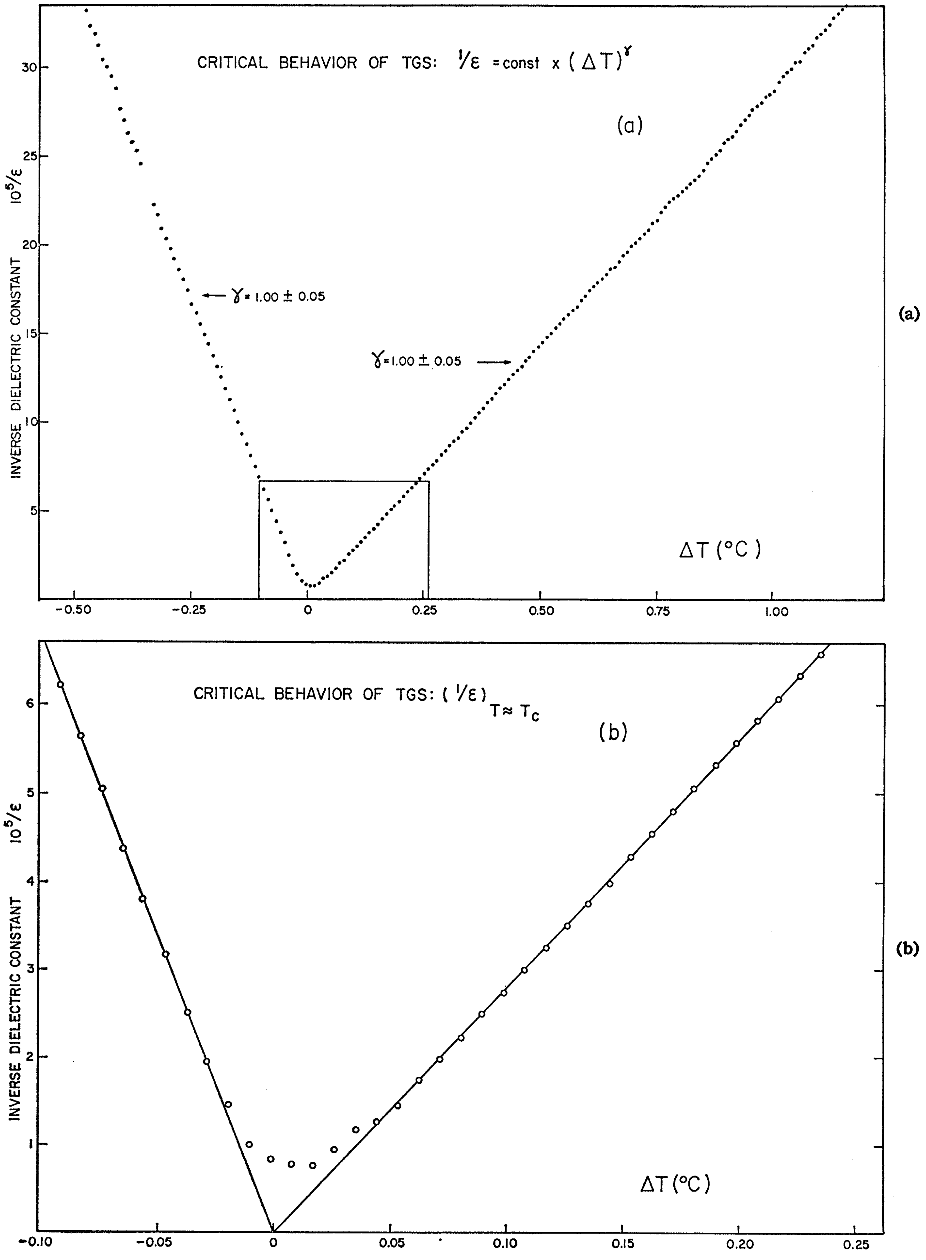

FIG. 2. (a) Plot of the inverse dielectric constant versus temperature ($T_c = 49.42 \pm 0.05$°C). (b) Detail of the same plot as in (a) (portion squared) in larger scale, showing behavior in the immediate vicinity of T_c.

agreement with the prediction of the thermodynamic theory, including adiabatic correction.[6,13] The value of C^+ is 3560°C. Present results on the behavior of ϵ near T_c seem to be somewhat different from those found by Craig.[9] We believe our sample might have fewer impurities or lattice defects.

V. SUMMARY AND DISCUSSION

The critical behavior of TGS has been studied through the temperature variation of spontaneous polarization and dielectric constant near T_c. This behavior can be accounted for by $P_s = \text{const}\times(\Delta T)^\beta$ and $1/\epsilon = \text{const}\times(\Delta T)^\gamma$, with $\beta = 0.51 \pm 0.05$ and $\gamma = 1.00 \pm 0.01$, in good agreement with the thermodynamic theory of ferroelectrics which predicts $\beta = \frac{1}{2}$ and $\gamma = 1$. The experimental values of β and γ from the present study do not appear to show parallelism with their analogs in second-order magnetic transitions.

It may be worthy of mention that the observed behavior of TGS in the critical region does not contradict the conclusions of the molecular field theory, in contrast with the experimental evidence for ferromagnetic transitions.

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Reflection and Transmission of Electromagnetic Waves by a Moving Dielectric Slab*

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The reflection and transmission of electromagnetic waves by a moving dielectric slab are investigated theoretically and the reflection and transmission coefficients are determined. Two cases of the movement are considered: (a) the dielectric slab moves parallel to the interface; (b) the dielectric slab moves perpendicular to the interface. Various interesting features concerning the variation of the reflection and transmission coefficients, angles of reflection and transmission, and the frequencies of the reflected and transmitted wave, as a function of the velocity of the moving medium, are discussed.

I. INTRODUCTION

THE effects of a perfectly reflecting moving boundary upon an incident plane electromagnetic wave were discussed many years ago by various authors.[1–3] The formula for the equivalent index of refraction of a dielectric medium moving at a uniform velocity with respect to a reference frame S, as viewed from the reference frame S, was first derived by Fresnel.[1–3] The well-known Fresnel formula was then verified experimentally by Fizeau. Sommerfeld gave a rather comprehensive treatment of these interesting problems in his book.[3] However, it is somewhat surprising to learn that the problem of the reflection and transmission of plane waves by a uniformly moving dielectric slab has not been treated.[4] The purpose of this paper is to present the solution to this important problem. The result shows that there exists no Doppler shift in frequency for the transmitted wave due to the movement of the slab. Furthermore, the sum of the reflection coefficient and the transmission coefficient is not unity in general. Discussion of these features as well as several other interesting features concerning the variation of the reflection and transmission coefficients, the angles of reflection and transmission, and the frequency of the reflected waves, as a function of the velocity of the moving medium will be given.

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