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Critical Fluctuations in Triglycene Sulfate*

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Critical-point polarization fluctuations in ferroelectric triglycene sulfate have been observed at the Curie temperature by measuring the random noise voltages appearing between electrodes applied to the crystal. These noise voltages are interpreted in terms of the Nyquist noise associated with the crystal conductance and therefore can be used to determine the true crystal impedance at and near the transition temperature where the crystal is highly nonlinear. The polarization noise density at the Curie point has a simple relaxation spectrum with a time constant of 5.3×10^{-3} sec, which furthermore is relatively independent of temperature near the Curie temperature. A thermal Barkhausen noise observed in barium titanate as the crystal is passed slowly through the transition temperature appears to be associated with the inherent domain structure of the sample.

I. INTRODUCTION

IT has been predicted[1] that large random fluctuations of polarization in ferroelectric crystals should occur at the Curie temperature if the ferroelectric transition is of second order. The phenomenon is analogous to the well-established pressure fluctuations which are visible as critical opalescence in a gas-liquid mixture at the critical point. Such critical polarization fluctuations have now been observed in single crystal triglycene sulfate and represent the first measurements of critical-point fluctuations in solids.

Polarization fluctuations are detected by measuring random voltages appearing between electrodes applied to the crystal. Because the specimen is in thermodynamic equilibrium during the measurement, this noise voltage can be related to Nyquist noise associated with the crystal conductance at the Curie temperature. Since the observed noise amplitude also depends upon crystal capacitance, noise measurements prove to be a very useful experimental technique for determining the effective resistivity and dielectric constant of the material near and at the Curie temperature. Such measurements are difficult to carry out by conventional impedance bridge techniques because of the highly nonlinear behavior of the crystal near the critical temperature.

Ferroelectric crystals which have first-order transitions, for example, barium titanate, do not exhibit critical-point fluctuations. In such specimens a polarization noise is observed when the sample is passed slowly through the transition temperature. This effect, which may be termed thermal Barkhausen noise, disappears when the crystal is in thermodynamic equilibrium and appears to be related to conventional Barkhausen noise.[2]

II. EXPERIMENTAL TECHNIQUE

Because of the very rapid variation of properties with temperature near the critical temperature in ferroelectric crystals, it is necessary to maintain accurate control of the sample temperature. In the present work specimens were mounted in a heavy copper block completely surrounded by 6 in. of thermal insulation contained in an electrically heated furnace. The thermal time constant of this arrangement was several hours. The furnace temperature was controlled and regulated with a servo system containing a dc amplifier and magnetic amplifier as sketched in the block diagram of Fig. 1. The reference temperature bath was a commercial self-contained servo system with an accuracy of ±0.01°C. The sample temperature was measured with a conventional potentiometer with respect to the same reference bath. With this apparatus it was possible to determine the sample temperature within ±0.01°C and to reduce the rate of change of temperature to less than 10^{-6} °C/sec.

The samples were prepared with evaporated gold electrodes on crystal faces perpendicular to the ferroelectric axes. The specimens were approximately 1 mm thick and mounted so that the mechanical strains were negligible. The noise voltages appearing across the electrodes (approximate area 0.1 cm^2) were applied to a load resistor external to the furnace and measured with a standard tunable amplifier-voltmeter. The system was calibrated using the Nyquist noise of the load resistors. For some measurements it proved convenient to record the mean-square noise level on a conventional chart recorder.

III. CRITICAL POLARIZATION NOISE

The second-order character of the transition at the Curie temperature in triglycene sulfate is well established.[3] The free energy can be written in terms of the polarization P as

$$F(P,T)=F(0,T)+A(T-T_0)P^2+BP^4+CP^6+\cdots, \quad (1)$$

where $F(0,T)$ is the polarization-independent part of the free energy, T_0 is the transition temperature, and A, B, and C are constants. In terms of the applied electric field E and the dielectric constant ϵ, the following thermodynamic equations apply

$$\partial F/\partial P=E, \quad \partial^2F/\partial P^2=4\pi/(\epsilon-1). \quad (2)$$

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[1] R. E. Burgess, Can. J. Phys. **36**, 1569 (1958).

[2] A. G. Chynoweth, Phys. Rev. **110**, 1316 (1958).

[3] S. Triebwasser, IBM J. Research Develop. **2**, 212 (1958).

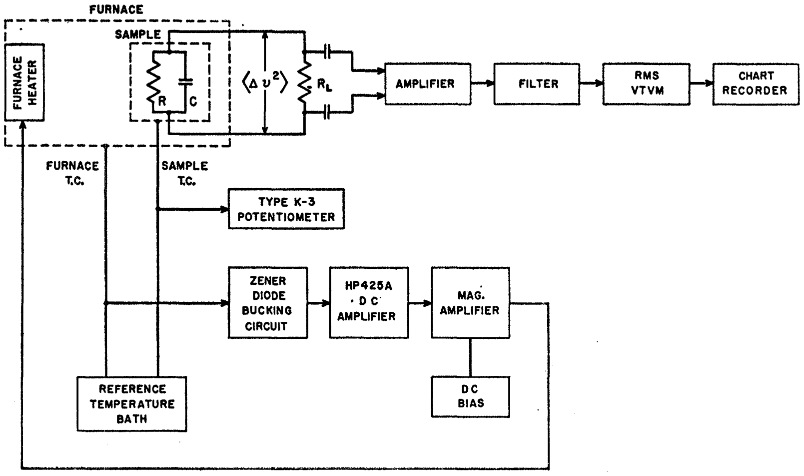

FIG. 1. Block diagram of temperature-control and noise-measuring apparatus.

From Eqs. (1) and (2), for zero applied field, the variation of the dielectric constant near T_0 is given by

$$4\pi/(\epsilon-1) = -4A(T-T_0) \quad \text{for } T<T_0 \text{ where } P\neq 0,$$
$$= 2A(T-T_0) \quad \text{for } T>T_0 \text{ where } P=0, \quad (3)$$

where the familiar 2:1 ratio in the slope of $1/\epsilon$ vs T near the Curie temperature is evident. Fluctuations in polarization can be specified by the variance of P, which is given by

$$\text{var}P = \frac{kT}{(\partial^2 F/\partial P^2)}. \quad (4)$$

According to Eq. (1), the second derivative of the free energy with respect to the polarization vanishes as T approaches T_0 so that var$P$ becomes infinite and very large polarization fluctuations are expected. A more critical analysis[1] indicates that the fluctuations at the Curie temperature are governed by the fourth derivative of the free energy.

Polarization fluctuation noise can be calculated using Nyquist's theorem since the crystal is in thermodynamic equilibrium. From the simple equivalent circuit shown in Fig. 1, the spectral noise voltage across the load resistor R_L is given by

$$\langle \Delta v^2 \rangle = \left(\frac{4kT_S}{R} + \frac{4kT}{R_L}\right) \Big/ \left[\left(\frac{1}{R} + \frac{1}{R_L}\right)^2 + (\omega C)^2\right], \quad (5)$$

where R and C represent the equivalent parallel resistance and capacitance of the specimen, and T_S and T are the sample and load resistance temperatures, respectively. The first term in the numerator of Eq. (5) is the short-circuit current noise due to the sample conductance, and the second term is that due to the load resistance. Since the polarization fluctuations can be related to the short-circuit noise current, evaluation of R is a convenient way of measuring the polarization noise. In order to determine both R and C the noise voltages, for two different values of R_L, can be used. The values are obtained from the simultaneous solution of two relations corresponding to Eq. (5) for different R_L values.

The observed noise voltages appearing across the load resistance at a frequency of 1000 cps for temperatures near the Curie temperature and for several different values of load resistance are shown in Fig. 2. These curves are taken from chart recordings of the noise output. For small values of R_L, the measured noise is dominated by the Nyquist noise of the load resistance when the sample temperature is sufficiently far from T_0 so that the crystal impedance is large compared to R_L. A noise minimum occurs at the Curie temperature where the crystal impedance becomes small compared to R_L even though, according to Eq. (4), very large polarization fluctuations are expected at T_0. This is because the internal impedance of the crystal decreases faster than the noise current increases as T approaches T_0. Therefore, a noise-voltage minimum is expected at the Curie temperature in agreement with Eq. (5). From the data

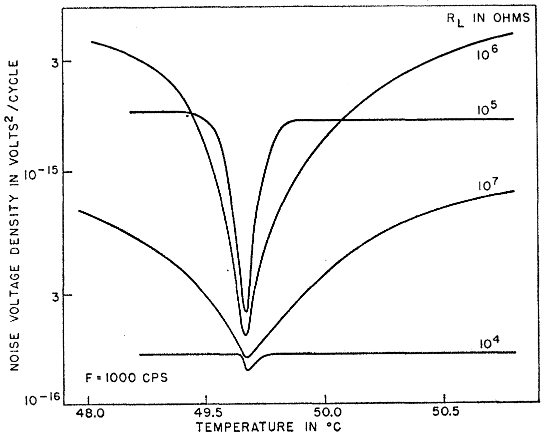

FIG. 2. Variation of noise voltage across the load resistor as a function of temperature of a triglycene sulfate crystal near the Curie temperature for several values of load resistor and at a frequency of 1000 cps.

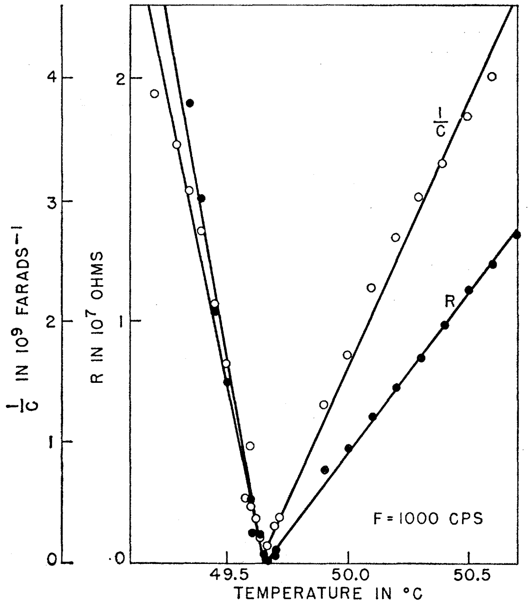

FIG. 3. Variation of the equivalent parallel resistance and capacitance near the Curie temperature as calculated from the data of Fig. 2.

of Fig. 2 the Curie temperature is 49.67°C which is in satisfactory agreement with published values.[3]

The sample resistance and capacitance calculated from the data of Fig. 2 are shown in Fig. 3. Good agreement between values calculated by taking all possible R_L pair combinations is obtained. Figure 3 shows the usual lambda point behavior of the capacitance characteristic of a second-order transition and indicates a similar variation of R with temperature. Using Eq. (3), the constant $A = 1.6\times10^{-3}(°\text{C})^{-1}$ is determined from the data both above and below T_0. This is in reasonable agreement with a published value[3] of $1.96\times10^{-3}(°\text{C})^{-1}$. Since, according to Fig. 3, both R and $1/C$ are inversely proportional to $T-T_0$, it appears that the RC time constant is independent of temperature near the Curie temperature. Time constants of 5.3×10^{-3} sec and 2.7×10^{-3} sec are obtained for temperatures below and above the transition temperature, respectively.

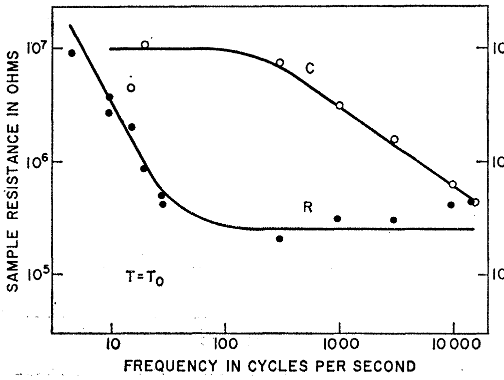

FIG. 4. Frequency behavior of the equivalent parallel resistance and capacitance for a triglycene sulfate sample at the Curie temperature.

From measurements similar to those of Fig. 2, the variation of R and C with frequency at the Curie temperature are obtained as shown in Fig. 4. Considering the difficulty of random-noise measurements over a wide dynamic range and broad frequency interval and that the calculation involves subtraction of two noise measurements, these data are remarkably consistent. The frequency dependence of R and C shown in Fig. 4 suggests that the parallel equivalent circuit representation, which is convenient for experimental measurements, should be converted to a series circuit containing elements which are frequency independent. It has been pointed out[1] that the equivalent circuit which represents the admittance of the crystal and its fluctuation properties consists of a vacuum capacitance c_g in parallel with a series combination of the dipole capacitance c and loss resistance r. The relations between the parallel- and series circuit parameters are easily shown to be

$$R=(1/c)[(1+\omega^2\tau_1^2)/\omega^2\tau_1], \tag{6}$$

$$C=c/(1+\omega^2\tau_1^2)+c_g, \tag{7}$$

where $\tau_1 = rc$.

The variation of R with frequency in Fig. 4 is in agreement with Eq. (6) and yields the values $c=2.2\times10^{-8}$ F, $\tau_1=5.3\times10^{-3}$ sec, and $r=2.4\times10^5\Omega(\rho=1.4\times10^3\Omega$ cm). The variation of C shown in Fig. 4 is in approximate agreement with Eq. (7) except that the high frequency experimental values are larger than predicted. On the other hand, the magnitude of the measured capacitance at low frequency agrees reasonably well with c determined from the parallel resistance. This result suggests that the simple series equivalent circuit may not be completely satisfactory at the Curie temperature. In this connection it is interesting that the RC time constant from Fig. 3 for $T<T_0$ is the same as τ_1 even though, according to Eqs. (6) and (7), $RC=1/\omega^2\tau_1$.

Since the noise current is the time derivative of the fluctuating polarization charge, the polarization noise density may be found from the expression

$$\langle\Delta i^2\rangle = A^2\omega^2\langle\Delta P^2\rangle = 4kT_S/R, \tag{8}$$

so that

$$\langle\Delta P^2\rangle = 4kT_S/A^2\omega^2R. \tag{9}$$

Using the data of Fig. 4 and Eq. (9), the polarization noise spectrum is as given in Fig. 5. The polarization noise is clearly a simple relaxation spectrum with a time constant given by τ_1. This implies that the loss mechanisms in the crystal at the Curie temperature can be represented by a simple relaxation process. Integration of the polarization noise spectrum over all frequencies results in a total fluctuation of $\text{var}P=6.2\times10^{-18}$ (C/m^2).[2] Also shown in Fig. 5 is the variation of the dielectric constant with frequency as calculated from measured values of C. The large value of the dielectric constant at the Curie temperature is evident. Since these are obtained in the absence of any applied voltage, they are presumably more characteristic of the crystal than those obtained using conventional measuring techniques.

IV. THERMAL BARKHAUSEN NOISE

Somewhat less detailed noise measurements have been carried out on barium titanate crystals near the transition temperature. The transition in barium titanate is of first order,[4] so that critical fluctuations are not expected in thermal equilibrium. The observed noise voltage must still be given by Nyquist's theorem, however, so that crystal parameters may nevertheless be determined from noise measurements. The present experiments have been concerned with large noise voltages which are observed as the crystal is passed slowly through the transition temperature under nonequilibrium conditions.

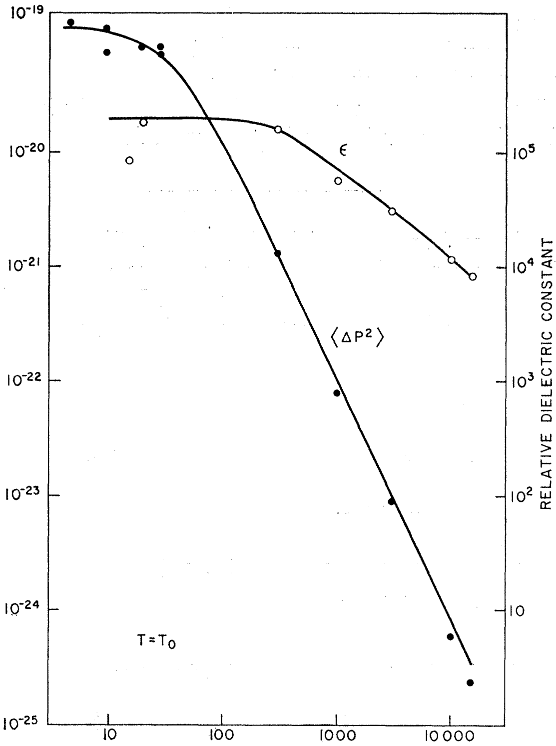

FIG. 5. Polarization fluctuations and dielectric constant of triglycene sulfate at the Curie temperature.

These large noise voltages occur at the transition temperature as shown by recorder traces of the noise amplitude at 1000 cps in Fig. 6 compared to the remanent polarization as determined from hysteresis-loop measurements. The thermal hysteresis indicative of a first-order transition is evident in both the remanent polarization and noise-voltage data. The magnitude of the peak-noise voltage is reasonably independent of the rate of change of temperature down to drift rates of the order of 10^{-3} °C/sec. At rates slower than 10^{-5} °C/sec, however, the large noise voltages are absent as indicated by the solid data points of Fig. 6. Similar noise peaks are observed at the transition temperature near 0°C.

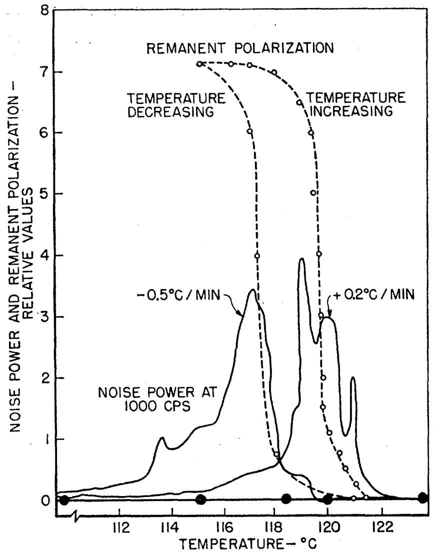

FIG. 6. Noise voltage and remanent polarization of a barium titanate crystal near the transition temperature. The solid data points refer to thermal equilibrium conditions.

The magnitude of the noise and much of the fine structure in the recording traces are quite reproducible upon subsequent passes through the transition temperature and the noise spectrum has been obtained in this fashion. The short-circuit current noise is given in Fig. 7 for transitions at 120 and 0°C. The spectra show a $1/f$ behavior at low frequencies and a trend toward white noise above about 10^3 cps. The difference in the noise magnitude between increasing and decreasing temperatures may be associated with the difference in the

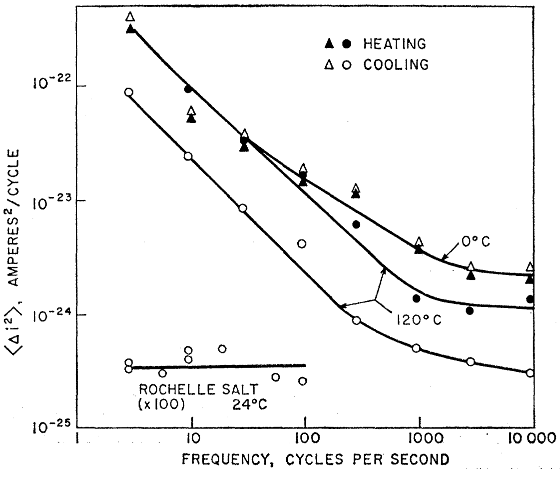

FIG. 7. Short-circuit current noise spectrum of thermal Barkhausen noise from barium titanate and Rochelle salt at the transition temperature.

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[4] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1957), p. 196.

dielectric constant on the two sides of the transition temperature. This effect is not present in the lower temperature transition, where the difference in the dielectric constants are less pronounced. Preliminary measurements on a Rochelle salt crystal indicate a white noise spectrum, but the noise level is too small to be measured accurately. The lower noise in Rochelle salt compared to barium titanate is consistent with the difference in the saturation polarization of the two materials.

These results suggest that the noise may be due to a thermal Barkhausen effect produced by the creation or destruction of polarized domains as the crystal passes through the transition temperature. At very slow temperature drift rates the interval between individual noise pulses becomes so long that the integrated noise level is small. If this interpretation is correct the data suggest that similar domain configurations are active at both the 120°C transition and the 0°C transition in barium titanate, since the noise levels are the same. The $1/f$ characteristic of the spectrum may imply an exponential distribution of domain sizes according to the conventional interpretation of $1/f$ noise.[5]

V. CONCLUSIONS

These experimental results appear to establish the existence of critical-point polarization fluctuations in ferroelectric crystals at the Curie temperature. The polarization fluctuations can be interpreted in terms of Nyquist noise associated with the crystal conductance and therefore noise measurements can be used to determine the true crystal impedance at and near the transition temperature. The fact that the polarization noise density in triglycene sulfate is a simple relaxation spectrum indicates that the loss mechanisms at the Curie temperature in this material can be characterized by a single relaxation time. It appears that this time constant is relatively independent of temperature near the transition temperature. Ferroelectric crystals having a first-order transition exhibit a thermal Barkhausen effect which may prove useful in examining the inherent domain size distribution in such crystals.

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[5] A. van der Ziel, *Fluctuation Phenomena in Semiconductors* (Academic Press Inc., New York, 1959), p. 56.

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Superconductivity of Chromium Alloys

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The superconducting properties of Cr-Ru, Cr-Rh, and Cr-Ir alloys have been investigated and the transition temperatures have been determined as a function of composition and of valence-electron concentration.

The Cr-Ru system contains three superconducting phases all of which have a homogeneity range. A hexagonal close-packed alloy containing 50 at. % Cr has a transition temperature of 1.65°K. The sigma-phase type compound Cr_2Ru has a transition temperature of 2.0°K and Cr_3Ru which crystallizes in the *β-W* type structure becomes superconducting at 3.3°K.

The hexagonal close-packed alloys in the Cr-Rh system are superconducting. The transition temperature of an alloy containing 70 at. % Cr is 1.1°K. Weak ferromagnetism was observed in cold-worked hexagonal close-packed alloys containing approximately 60 at. % Cr.

There are two superconducting phases in the Cr-Ir system. A hexagonal close-packed alloy containing 72 at. % Cr has a transition temperature of 0.83°K. An alloy with the *β-W* type structure containing 85 at. % Cr becomes superconducting at 0.77°K.

Both superconductivity and ferromagnetism occur in the Cr-Ir system. The critical conditions for the occurrence of both phenomena are discussed.

INTRODUCTION

THE only reported superconductors containing chromium are the solid solutions of chromium in hexagonal and in cubic titanium.[1] Chromium and molybdenum are in the same column of the periodic table and form many isomorphous compounds and intermediate phases with the noble metals of the VIIIth column. Recently, molybdenum has been reported as a superconductor[2] and many of the molybdenum alloys are known superconductors.[3] For the latter reason, a study of the superconducting properties of Cr alloys was undertaken.

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[1] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1959).

[2] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters **8**, 313 (1962).

[3] B. T. Matthias, Phys. Rev. **97**, 74 (1955).