INVESTIGATION OF ELECTROCALORIC EFFECTS IN FERROELECTRIC SUBSTANCES

Status Report No. 4

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PERSONNEL

Project Supervisor: Gordon G. Wiseman

Graduate Student Assistants: Richard J. Brincks, Joe A. Hostetter, and Robert G. Spahn.

(NSF Trainee, Robert W. Manweiler, helped with this work.)

DEFINITION OF TERMS AND SYMBOLS

Rationalized MKS units are used throughout. Thermodynamic formulas such as $dU = TdS + Xdx + EdP$ are written for a unit volume of material. This procedure is not exactly proper because the thermodynamic system (the experimental crystal) changes its volume slightly, but only inappreciable errors result.

C = Curie constant. Curie-Weiss Law is $\chi = C/(T - T_p)$.

c_E = Specific heat at constant field (and zero stress).

c_P = Specific heat at constant polarization (and zero stress).

D = Electric displacement. $D = \epsilon_0 E + P$.

E = Applied electric field.

G_1 = Elastic Gibbs function. $G_1 = U - TS - xX$

G_{10} = G_1 at some (arbitrary) reference temperature.

p = Electric dipole moment.

P = Electric polarization per volume. P_S is the spontaneous
   electric polarization per volume.

p^E = Pyroelectric coefficient at constant field (and stress).

S = Entropy per volume.

T = Temperature in degrees Kelvin.

T_c = Critical temperature (loosely speaking, either T_f or T_p).

T_f = Ferroelectric Curie temperature = the temperature at which
   P_S disappears when the substance is heated.

T_p = Paraelectric Curie temperature as defined by the Curie-
   Weiss Law, $\chi = C/(T - T_p)$.

U = Internal energy per volume.

X = Applied stress. (Tensile stress has a positive sign.)

x = Strain. (Elongation has a positive sign.)

ε_0 = Electric permittivity of vacuum = 8.85 x 10^{-12} coul^2/n·m^2.

ζ = Devonshire's sixth-order coefficient (of P^6) in G-expansion.

ξ = Devonshire's fourth-order coefficient (of P^4) in G-expansion. (ψ appears as a misprint in place of ξ in Eq. 7 and 9 of Status Report No. 1.)

ρ = Mass density.

χ = Electric susceptibility. dP = $\varepsilon_0\chi$dE. The symbol χ may carry subscripts such as p (paraelectric), or superscripts such as T (constant temperature), X (constant stress), etc.

ψ = The non-linear polarization function in the Devonshire expansion. Usually written $\psi(P)$.

ψ' = The derivative of $\psi(P)$ with respect to P. Usually written $\psi'(P)$.

ω = Devonshire's second-order coefficient (of P^2) in G-expansion.

Note: Equations in the two Status Reports are numbered in order beginning with those in Status Report No. 1.

SUMMARY OF PREVIOUS STATUS REPORTS [1, 2, & 3]

Status Report No. 1 contained a thermodynamic description of the electrocaloric effect, the pyroelectric effect, and the relationship between them.[1] It was shown that the same crystalline properties give rise to both effects and that the relevant thermodynamic coefficients can be determined from electrocaloric measurements. So-called "tertiary effects" which arise from inhomogeneous temperatures or fields can be so large at to mask the

"real" effects; the tertiary effects are more easily eliminated
in the electrocaloric than in the pyroelectric measurements.

The apparatus and techniques that were devised for accu-
rately regulating the temperature of the experimental chamber
and making simultaneous measurements of the changes in electric
polarization and temperature that occur with changes in applied
field where described.

Status Report No. 2 included an account of the measurements
of the electrocaloric effect in KH_2PO_4 over the temperature
range from 78°K to 136°K. Numerical values for the pyroelectric
coefficient and its variation with temperature were determined
from the measured electrocaloric effect. Reliable values for the
Devonshire coefficients could not be determined from the electro-
caloric effect because their determination depends upon measured
values of changes in polarization, and the polarization of KH_2PO_4
is nearly saturated in the nearly-reversible tail of the hyster-
esis loops where the electrocaloric measurements are valid.
(E.g., see Fig. 4 of Status Report No. 2.)

Report No. 3 describes the changes made in the apparatus and
techniques that permitted electrocaloric measurements of $\Delta T/\Delta P$ in
the nearly-reversible tails of the hysteresis loops (i.e., in the
"saturation" region). These were the use of (1) a well-regulated,
high-voltage d-c power supply, (2) a much more sensitive d-c am-
plifier with a much higher input resistance for measurements of
polarization, and (3) a charge-biasing procedure to suppress the
zero of the charge-measuring equipment.

The degree of reversibility of the electrocaloric effect in the tails of the hysteresis loops for potassium dihydrogen phosphate was observed, and electrocaloric measurements of both $\Delta T/\Delta P$ and $\Delta T/\Delta E$ were made of this substance over the entire temperature range for which the electrocaloric effect is appreciable (77°K to 136°K). Maximum sensitivity for low-impedance pyroelectric detectors used in the ferroelectric state is not obtained until the applied biasing field is sufficiently large to bring the specimen into the nearly-reversible tail of the hysteresis loop. When operated in the paraelectric state, the pyroelectric coefficient can be controlled at will by a suitable biasing field, the sensitivity increasing with the field.

A relatively simple expression was found which gave a good fit to measured values of $(\Delta T/\Delta P)_S$ over the entire temperature range right through the Curie temperature. It is

$$(\partial E/\partial P)_T = (\rho c_p/T)(\Delta T/\Delta P)_S = 3.63 \times 10^7 P - 4.80 \times 10^{12} P^5.$$

However, we did not succeed in finding a Gibbs function G_1 that accurately describes both the ferroelectric behavior and the pyroelectric coefficient over the entire range of temperature.

The variation with temperature and field of an inner field coefficient γ that can be used to describe the spontaneous polarization and the electrocaloric effect was determined.

A computer program using Fortran IV was written for an IBM 7040 computer; its use vastly increased the speed and accuracy of some of the tedious computations and curve-plotting.

LIST OF EQUATIONS

A list of the most important equations from previous reports is given below. Equations are numbered consecutively, beginning with the first report.

$$dU = TdS + Xdx + EdP \tag{1}$$

$$dT = (T/\rho c_p)(\partial E/\partial T)_p dP \tag{2}$$

$$dT = (T/\rho c_E)(\partial P/\partial T)_E dE \tag{4}$$

$$P = f(a) = f[p(E+\gamma P)/kT] \tag{5}$$

$$dT = (\gamma/\rho c_p)PdP \tag{6}$$

$$dG_1 = -SdT - xdX + EdP \tag{7}$$

$$G_1 = G_{10} + \omega P^2/2 + \xi P^4/4 + \zeta P^6/6 \tag{8}$$

$$(\partial G_1/\partial P)_T = E = \omega(T)P + \xi P^3 + \zeta P^5 \tag{9}$$

$$dP = p^{X,E}dT \quad \text{where } p^{X,E}(\partial P/\partial T)_{X,E} \tag{20}$$

EXPERIMENTAL PROCEDURE

Single crystals of triglycine sulfate $(NH_2CH_2COOH)_3 \cdot H_2SO_4$ (abbreviated TGS hereafter) were obtained from the Clevite Corporation. Other TGS crystals were grown in this laboratory, but were not used to obtain the data presented here. A single crystal (rather than a sandwich) was used with major faces oriented perpendicularly to the monoclinic b axis (the two-fold polar axis). The major faces of the crystal were coated with air-dried silver paste and the crystal mounted, complete with a copper-constantan thermocouple, in the manner described in previous reports.[1,2,3] Some important properties of this crystal are tabulated below:

Area of major surfaces	2.82 cm^2
Thickness	3.19 mm.
Density	1.68 g/cm^3
Crystal symmetry (above T_c)	Monoclinic
Ferroelectric axis	Monoclinic b

$C_p = 419 + 1.747T$ joules/kgm^3 (interpolated from Ref. 4)

Triglycine sulfate undergoes one second-order ferroelectric transition at 322.60°K (49.45°C). Its dielectric properties have been investigated by Hoshino[4] and others[5]. Its use as a pyroelectric detector has been considered by the Sperry group[6,7] and by Chynoweth[8]. At each temperature, before any readings were taken, the crystal was cycled several times over the range of electric field to be used. Then equal step-wise changes in electric field were applied at one-minute intervals, and simultaneous changes in electric polarization and temperature were recorded on

a pair of 11-inch strip-chart recorders.[1,2,3] More than one complete hysteresis cycle was traversed step-wise at each temperature, but not all of these steps were used for the computations. Twenty-eight separate runs at established base temperatures were made, some of which were re-runs at a previously-observed temperature. The range of temperatures studied was from 273°K to 334°K. All together, the results of 2,335 field steps were recorded.

GENERAL DESCRIPTON OF RESULTS

The typical dielectric and electrocaloric behavior observed in TGS in the paraelectric region is shown in Fig. 1.

The temperature scale, ΔT, represents the cumulative step-wise electrocaloric changes in temperature. The error of closure for the cycle conveys an idea of the accuracy of the temperature measurements. Note that the electrocaloric effect appears to be a quadratic function of both E and P.

Below the Curie temperature, in the ferroelectric region, the electrocaloric effect appears to be not quadratic but approximately linear in E as shown by the typical results displayed in Fig. 2.

During the course of these experiments, several incidental but notable characteristics of TGS were observed. In the first place, the electrocaloric effect is asymmetrical with respect to the direction of the applied field. The asymmetry disappears above the Curie temperature but reappears again in the same direction but not in exactly the same amount when the crystal is
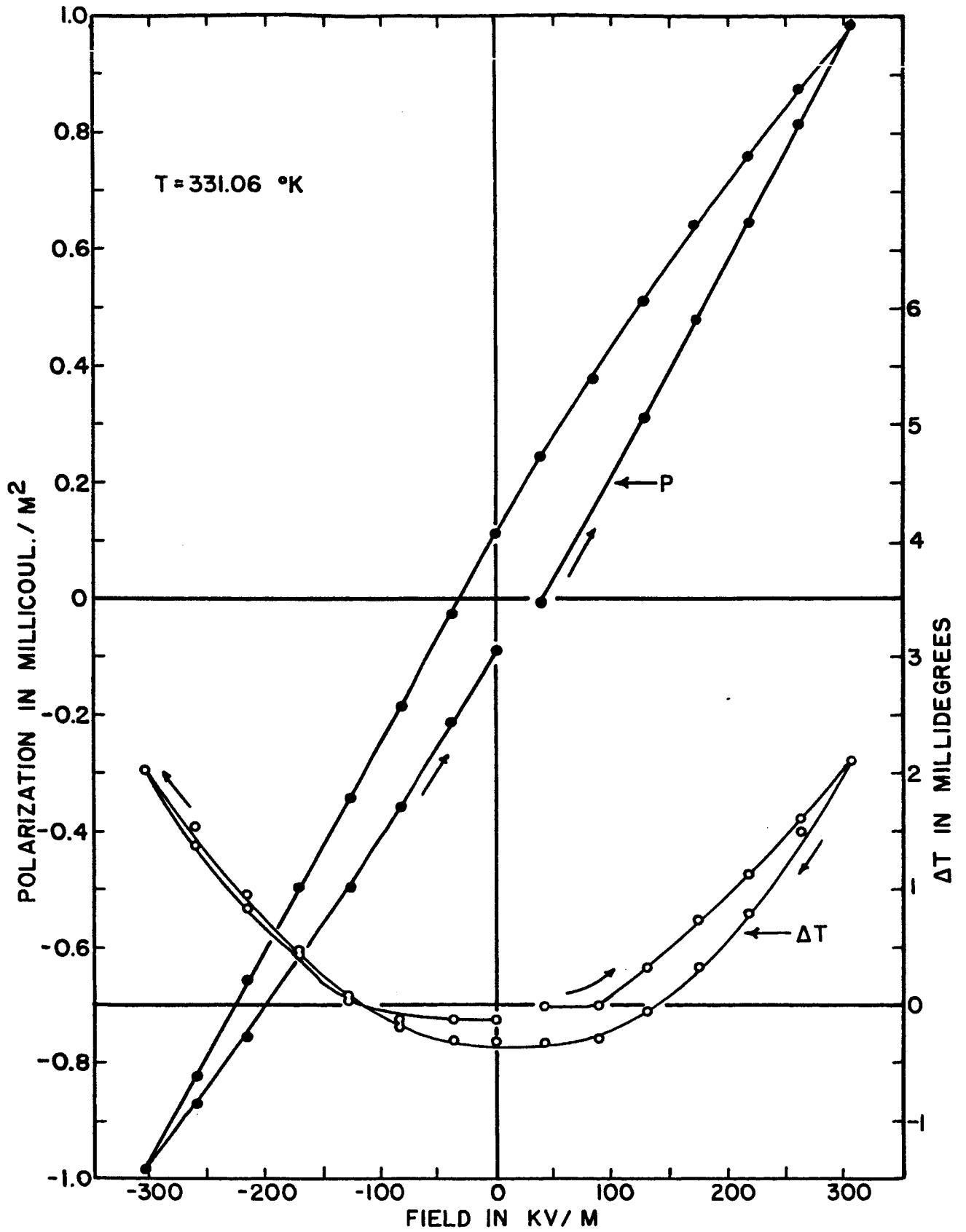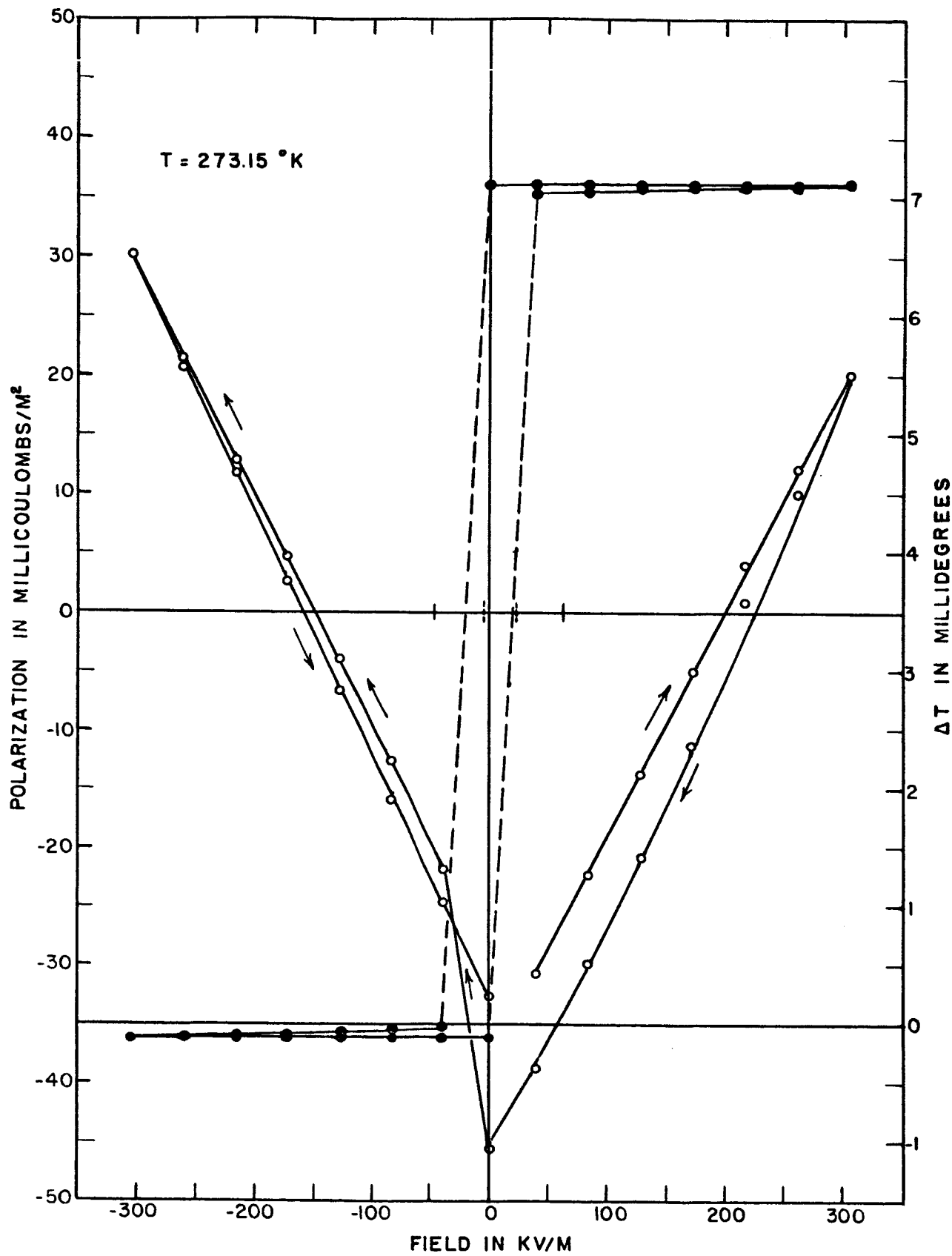
FIG. I. TGS ABOVE THE CURIE TEMPERATURE

FIG. 2. TGS BELOW THE CURIE TEMPERATURE

re-cooled. Secondly, the dielectric behavior is asymmetrical. Two effects seem to be involved here. One is the ordinary ferro-electric polarization -- its asymmetry is difficult to appraise because of unknown biasing charges residing in or on the crystal. The other is the relatively slow drift of charge that accompanies each change in applied field: each field step produces an initial rush of polarization (nearly "instantaneous" on the strip-chart recorder) which is followed by a gradually-slowing drift. The rates and magnitudes of these drifts are different for the two directions of applied field. These drifts appear to be a combination of ferroelectric relaxation polarization and ohmic conduction within the crystal. Similar asymmetry in the dielectric behavior of TGS has been observed by Hoshino[4] and by Chynoweth[8], the latter having observed asymmetry in the pyroelectric effect as well.

These relaxation effects are particularly vexing to us because they preclude accurate determinations of the "instantaneous" changes in polarization ΔP from our recorder trace. Electrocaloric effects (or possible irreversible heating) associated with these slow drifts are negligible, but our results have unusually large uncertainties in those quantities that involve measurements of ΔP; these inconsistencies were many times larger than those obtained with KDP or Rochelle Salt. Moreover, discrepancies several times as large as those attributable to faulty judgement in separating out the "instantaneous" part of ΔP occurred when attempts were made to repeat the results obtained at a previously-studied temperature; that is, the properties of the crystal

changed with use, its behavior becoming somewhat more consistent
and $\Delta T/\Delta P$ tending (with exceptions) to become greater.

As a result of these relaxation effects, the apparent value
of the coercive field for TGS is strongly dependent upon the fre-
quency of the applied field (or the duration of the field steps)
and upon the maximum field applied. Fig. 3 is a tracing of a
60-cps hysteresis loop taken at 273°K for comparison with Fig. 2.
It illustrates the asymmetry in the coercive field, the saturation
field, and the shape of the switching trace. These effects are
made abnormally evident in the photograph by applying barely
enough field to show the reversible regions -- at higher fields,
the 60-cps loops appear to be normal. For comparison, the coer-
cive field for the 60-cps loop and for a step-wise loop taken at
1 step/5 min are shown on Fig. 2 by the small vertical solid and
broken lines respectively.

Fig. 4 shows the total electrocaloric effect observed at
various temperatures. The upper curve represents the cumulative
sum of the individual electrocaloric temperature changes for a
maximum applied field of 305.6 kv/m, and the lower curve repre-
sents the values for a field of 128.4 kv/m.

Fig. 5 shows the variation with temperature of the polariza-
tion at maximum field P_{306} and at zero field P_0. These were ob-
tained from the cumulative step-wise changes. P_0 is the residual
polarization at zero field rather than the value obtained by
extrapolating the tips of the hysteresis loops to zero field;
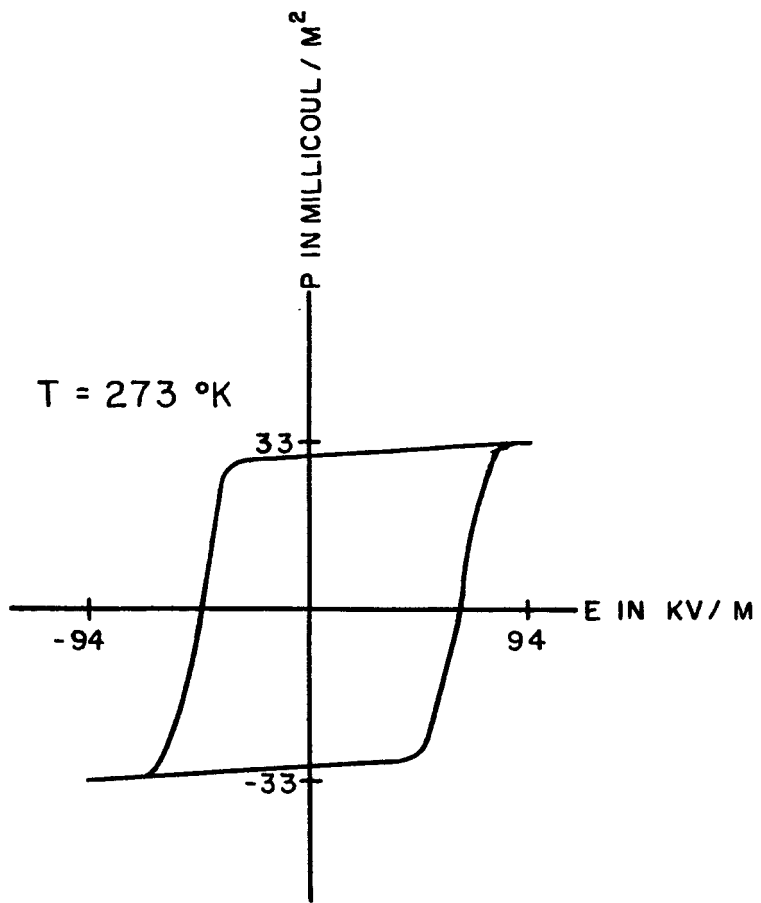such a value which for many substances can be taken to be the

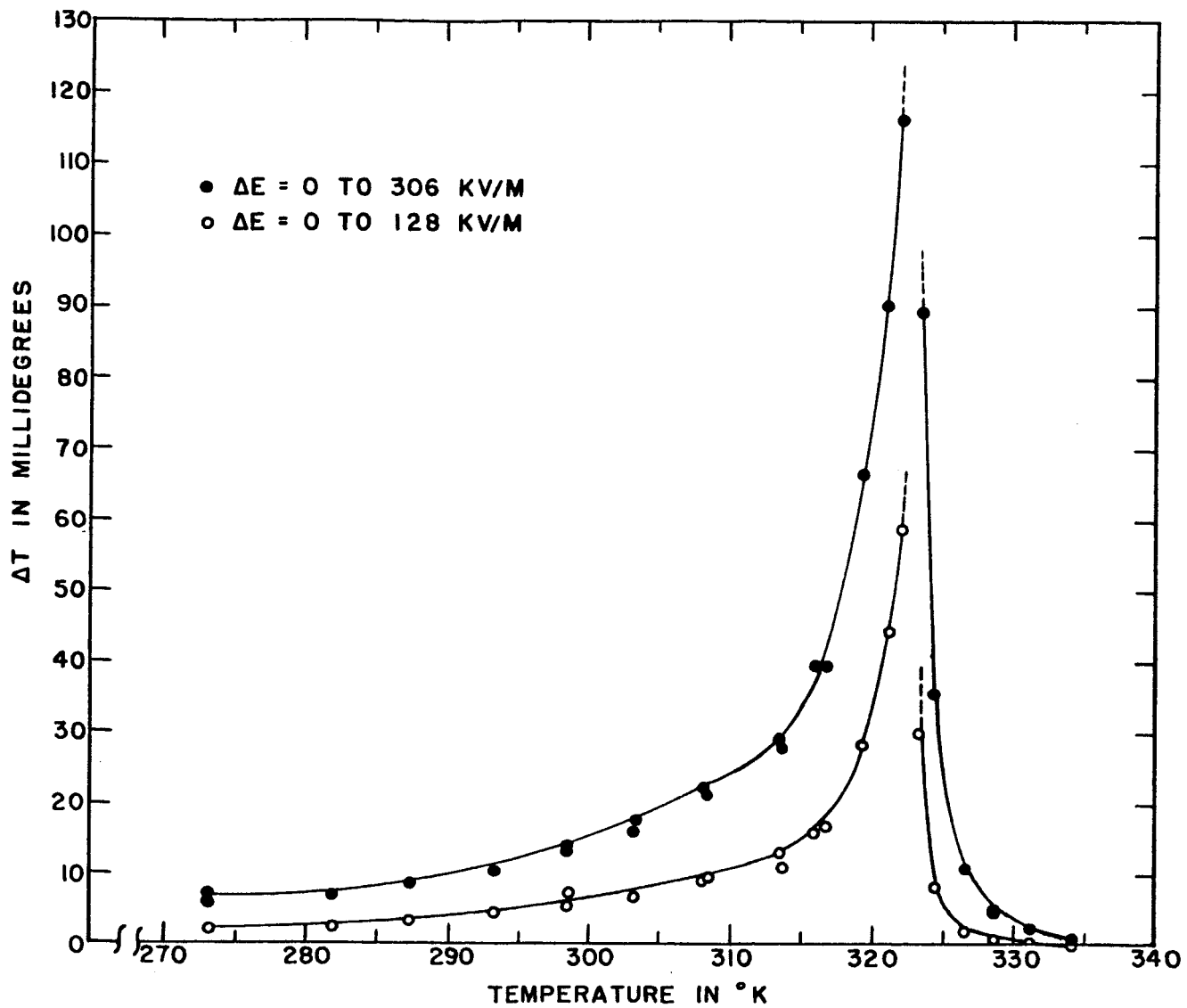FIG. 3. HYSTERESIS AT 60 CPS, BELOW CURIE TEMPERATURE
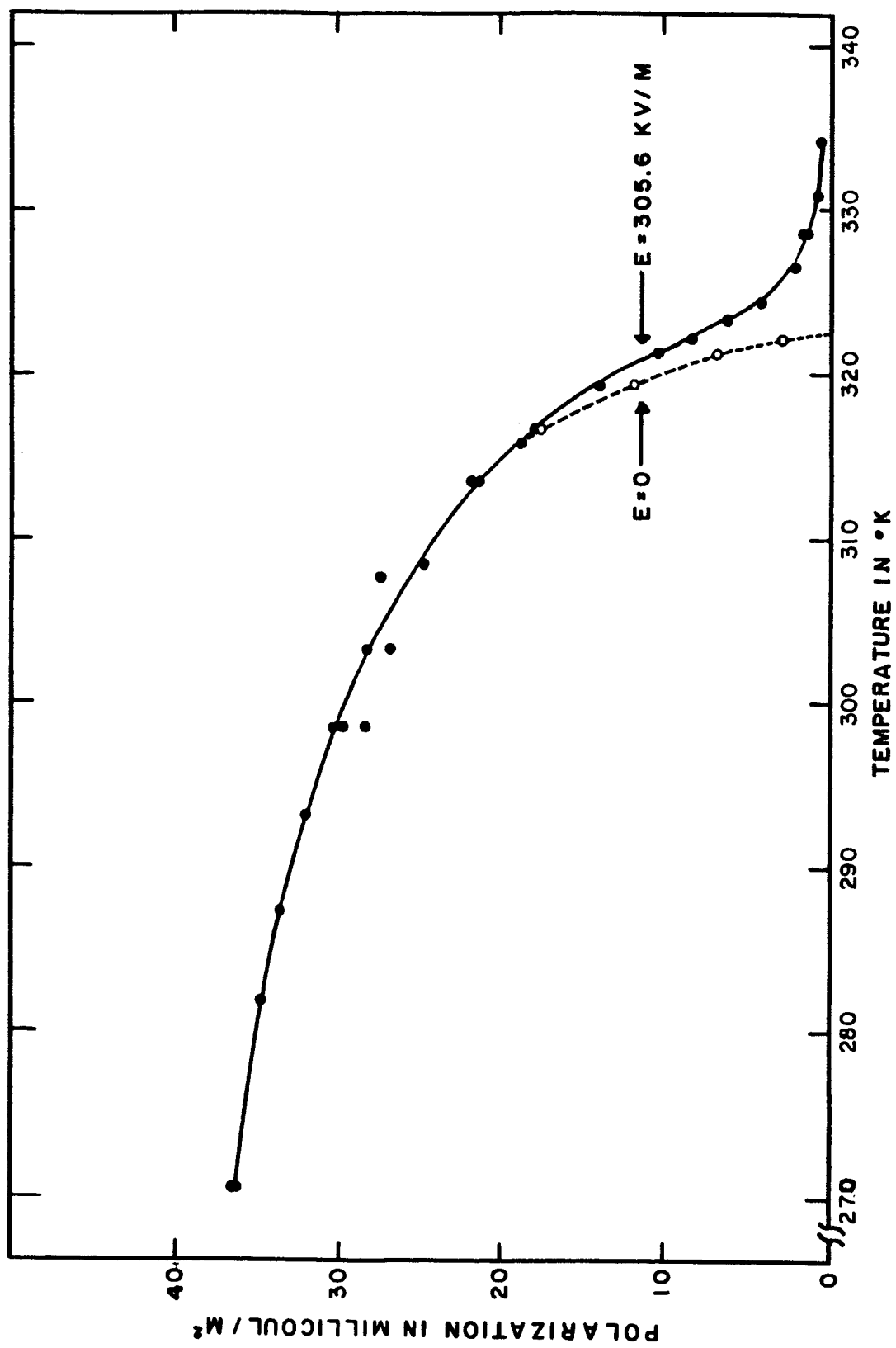
FIG. 4. TOTAL ELECTROCALORIC EFFECT IN TGS

FIG. 5. POLARIZATION OF TGS

spontaneous polarization has little meaning for TGS because at temperatures far below the Curie temperature P_o and P_s are indistinguishable on the scale of Fig. 5. At temperatures close to the Curie temperature, P vs E is a smooth curve with no flattening near the tips of the hysteresis loops.

The scattering of the points is due primarily to the aforementioned changes in the properties of the sample during the course of the work. Even so, the average curve drawn is reasonably consistent with the behavior usually cited as typical.

Fig. 6 shows the variation of the reciprocal static dielectric susceptibility (or rather $\Delta E/\Delta P$) with temperature above the Curie temperature as determined from the slopes of the plots of P vs E near E = 0. The solid line represents a Curie-Weiss law for T_c = 322.6°K (49.45°C) and C = 3260. Both of these values are in reasonable agreement with published determinations of the same quantities by a-c methods; the most recent measurements are those of Gonzalo[9] who gives T_c = 49.42°C and C = 3560. Hoshino[4] reports T_c = 48°C and C = 3280. This agreement with the Curie-Weiss law in the paraelectric region and the lack of a discontinuity in the spontaneous polarization P_s at the Curie temperature are characteristics of a second-order phase transition.
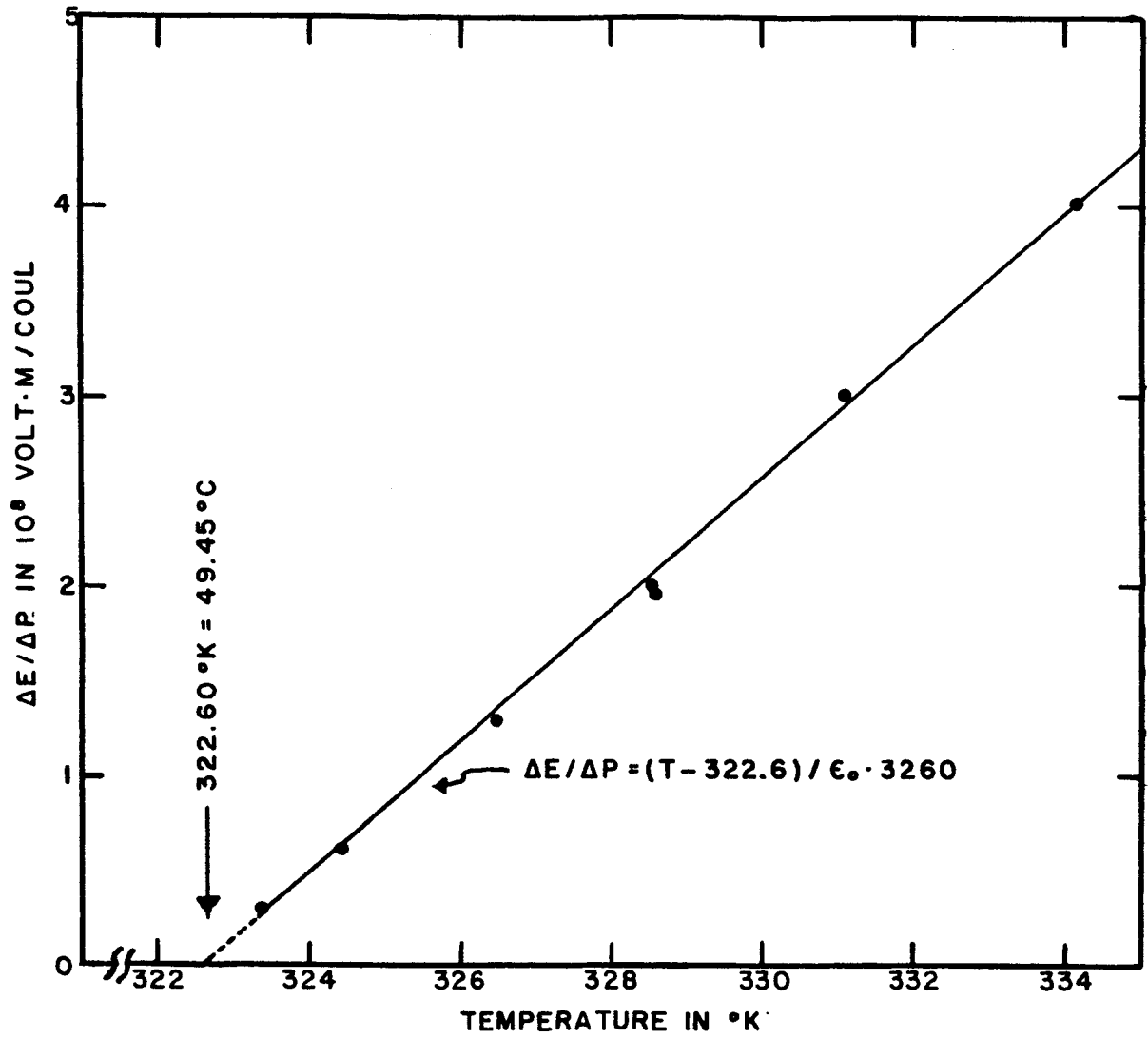
FIG. 6. RECIPROCAL D-C SUSCEPTIBILITY OF TGS

THERMODYNAMIC DESCRIPTION OF RESULTS

The "dP Form" of the Electrocaloric Equation

The thermodynamic theory of Devonshire can be used as a framework for describing the results of the electrocaloric measurements of TGS. Consider the "dP form" of the electrocaloric equation,

$$dT = (T/\rho c_p)(\partial E/\partial T)_p \; dP. \tag{2}$$

One would expect to be able to evaluate $(\partial E/\partial T)_p$ from Eq. (2) directly by measuring all of the other quantities including the electrocaloric effect $\Delta T/\Delta P$ and then obtain an equation of state, $E = f(T,P)$, simply by integration. The difficulty with this method is that the electrocaloric measurements (or any others for that matter) cannot be measured at arbitrarily-selected values of P; in particular, values of P smaller that P_s are not experimentally accessible below the Curie temperature, and values of P corresponding to low values of applied field are not thermodynamically reversible. (Because of the long reversible tails on the hysteresis loop of TGS, irreversibility was not a major problems with TGS. It was a major problem with potassium dihydrogen phosphate.)

One recourse is to assume a physically reasonable expression for the equation of state (or for the elastic Gibbs function from which an equation of state can be obtained by differentiation) and then compare the calculated values for the electrocaloric effect with the experimental values.

A frequently-used expression for the elastic Gibbs function G_1 for a substance which undergoes a second-order ferroelectric transition is[1]

$$G_1 = G_{10} + \omega P^2 + \xi P^4/4 + \zeta P^6/6 + \cdots . \tag{8}$$

Since $G_1 = -SdT - xdX + EdP$ and since the stresses X on the crystal are negligible, the field $E = (\partial G_1/\partial P)_T$ becomes

$$E = \omega P + \xi P^3 + \zeta P^5 + \cdots \tag{9}$$

so that for small electrocaloric temperature changes, Eq. 2 yields

$$\Delta T = (T/\rho c_p)[(\partial \omega/\partial T)(\Delta P^2/2) + (\partial \xi/\partial T)(\Delta P^4/4) + \cdots]. \tag{10'}$$

Our measured values of the electrocaloric temperature changes were compared to Eq. (10') by curve-plotting. The main problem above T_c is due to the aforementioned relaxation effects and ohmic drift which preclude accurate measurements of ΔP. Below T_c the relaxation effects are somewhat less, but the values of ΔP are small, P changing by only 2.1% over the entire range from $E = 0$ to $E = 305.6$ kV/m as would be seen in Fig. 2 if the scale could be blown up enough. It is for this reason that the reversible tail of each hysteresis loop was traversed step-wise several times with greatly increased sensitivity, a suitable large biasing charge being applied to keep the readings on scale. The polarization near $E = 0$ is not reversible, so readings at very low fields were not made.

Cumulative values of ΔT vs P^2 were plotted over the entire range of temperatures (273°K to 334°K), and it was found for the most part that only the first term in Eq. (10') seems to be

needed to give a reasonable fit to the data both above and below
the Curie temperature as illustrated by Figs. 7, 8, and 9. The
data for Fig. 7 were taken at the next-to-the-highest temperature
employed. (At the highest temperatures the electrocaloric effects
were too small, approximately 0.16×10^{-4} deg/step, to give con-
sistent data.) At successively lower temperatures, but still
above the Curie temperature, the plots became more consistent and
more linear (in P^2). The data for Fig. 8 were taken just below
the Curie temperature, and those for Fig. 9 were taken at the low-
est temperature employed. At lower temperatures the curves tend
to become concave upwards for lower values of E. This deviation
from linear behavior in P^2 suggests irreversible heating effects.
Linear behavior in P^2 is consistent with the usually-cited thermo-
dynamic expressions of Devonshire and others (see Ref. 5) in which
ξ and ζ are independent of temperature. On the other hand, Gon-
zalo[9] proposes a statistical theory in which ξ and ζ are propor-
tional to the absolute temperature. With our enhanced sensitivity
and charge-biasing technique, we consistently observe considerable
deviation from linearity in P vs E even near the tips of the hys-
teresis loops. Further study is required to determine whether
this deviation from linearity can be measured to sufficient accu-
racy to determine $\xi(T)$. In short, the electrocaloric data only
suggest that ξ is temperature dependent; the inaccuracies due to
relaxation effects and ageing of the specimen preclude definite
conclusions.

The combined results from all of the plots of ΔT vs ΔP^2 are
shown in Fig. 10. The values actually shown here were determined
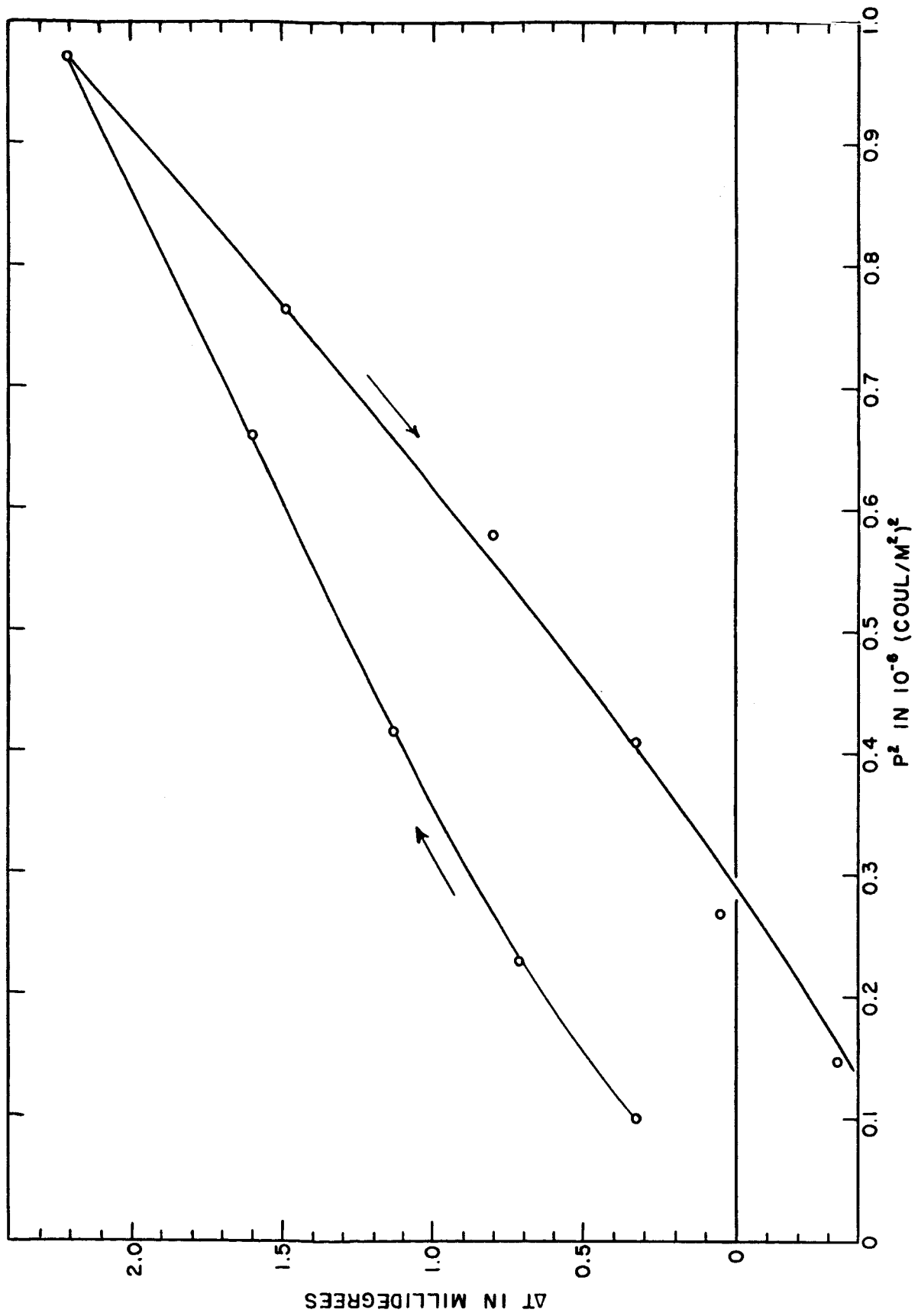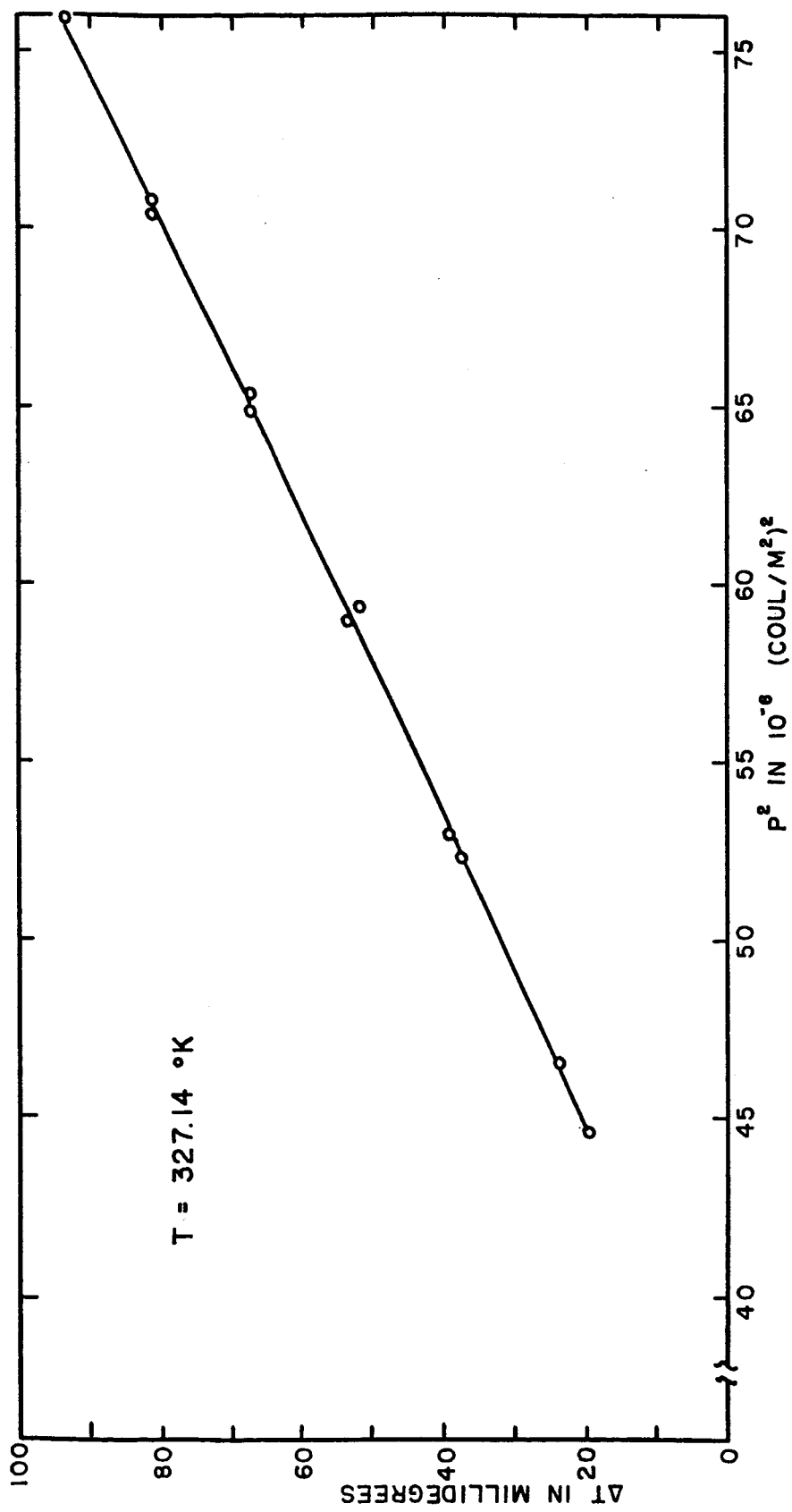
FIG. 7. ΔT vs P² 8.46 °K ABOVE T_c

T = 327.14 °K

ΔT IN MILLIDEGREES

P^2 IN 10^{-6} $(COUL/M^2)^2$

FIG. 8. ΔT VS P^2 AT 0.46 °K ABOVE T_c
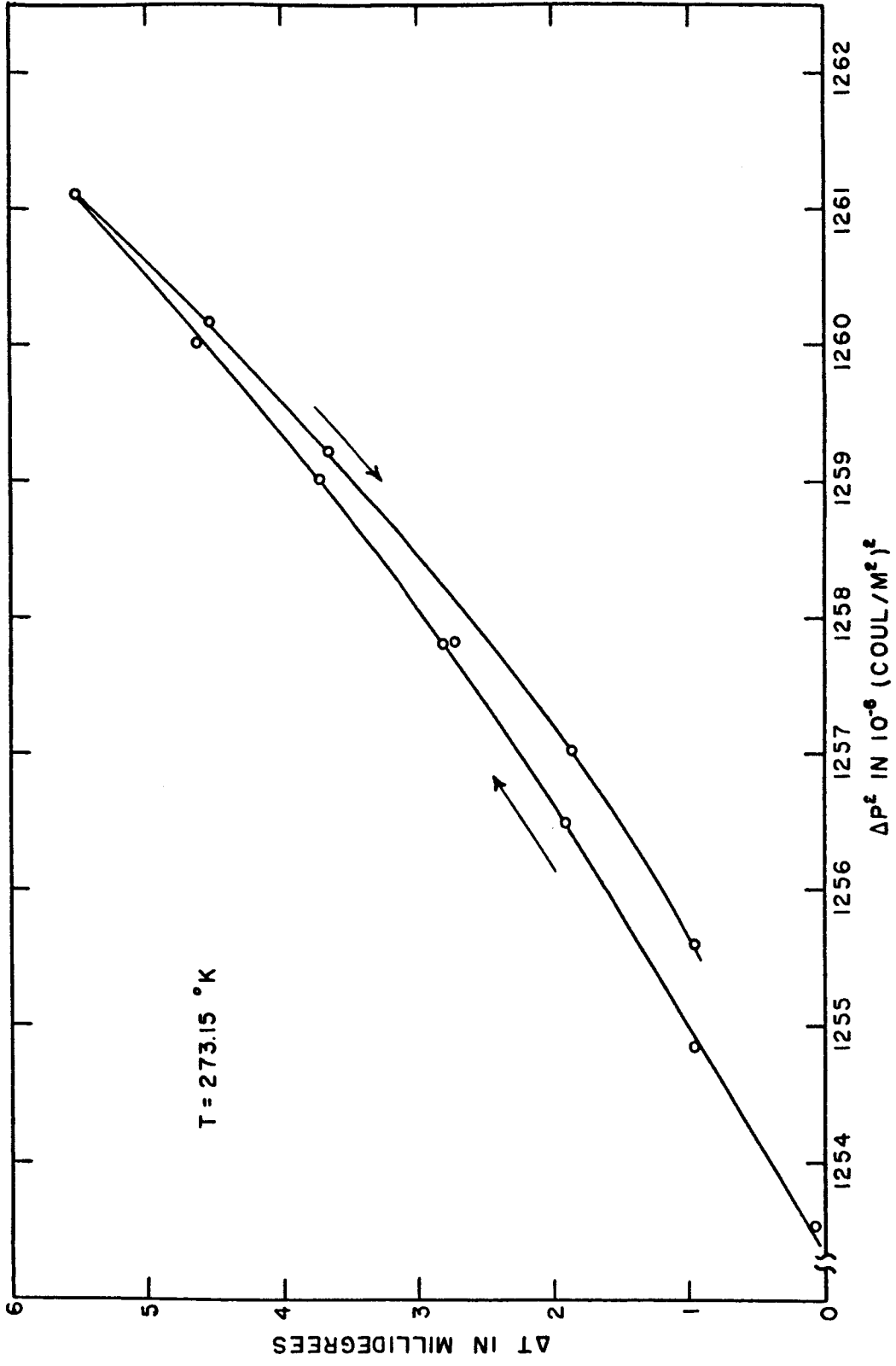
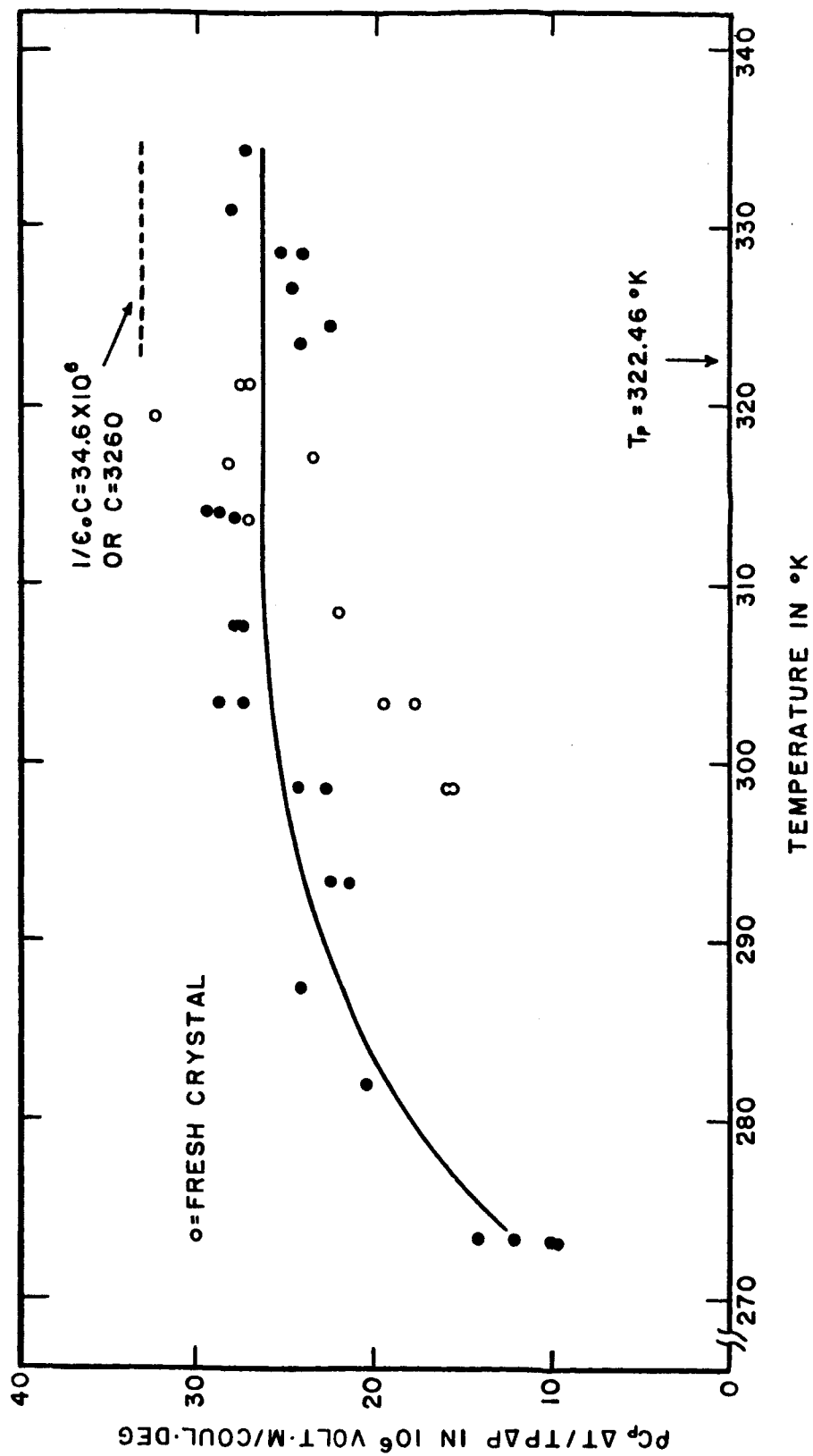FIG. 9. ΔT vs P² 49.45 °K BELOW T_c

FIG.10. VALUES OF ($\rho C_p \Delta T / T_P \Delta P$) AT 261 KV/M

by the computer and they consist of the mean slope, $\Delta T/\Delta P^2$, of the two field steps just preceding and just following the maximum value of E. The average value of E for these determinations was 261.2 kv/m. The values indicated by the open circles were obtained with a "fresh" crystal before the specimen had been heated above the Curie temperature for the first time, and these values ere given less weight in drawing the solid line.

Of course the scatter of points in Fig. 10 is disappointing. This scatter is due partly to the relaxation effects which make consistent readings of polarization difficult, but it is due mostly to actual changes in the properties of the crystal that are produced by the electrical and thermal treatment of the crystal specimen. Such uncertainties notwithstanding, two conclusions can be drawn: (1) there is no abrupt discontinuity in the quantily $\partial\omega/\partial T$ upon passing through the Curie temperature, and (2) the value of $\partial\omega/\partial T$ begins to drop appreciably at lower temperatures.

This continuity in the value of $\partial\omega/\partial T$ through the Curie temperature is greatly different from the behavior observed with potassium dihydrogen phosphate.[3]

As shown by information contained in Figs. 1 and 6, triglycine sulfate obeys the Curie-Weiss law so that Eq. (9) reduces to $E = \omega P = (T-T_p)P/\varepsilon_0 C$ above the Curie temperature. Consequently, ω is known to be zero at the Curie temperature, and $\omega(T)$ can be obtained from Fig. 10 by integration. The results of such an integration are displayed in Fig. 11.
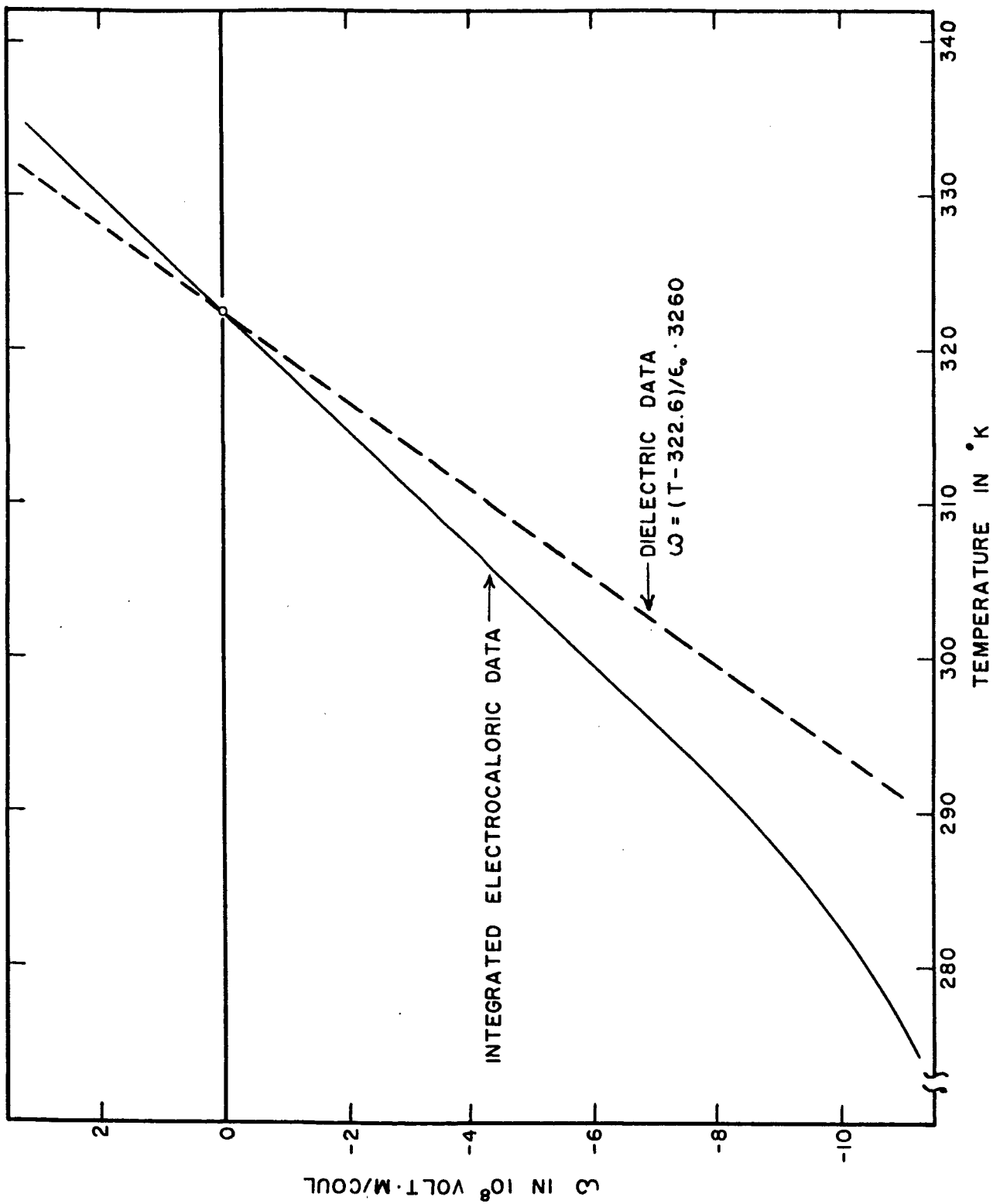
FIG. II. $\omega(T)$ FROM ELECTROCALORIC AND DIELECTRIC MEASUREMENTS

The Pyroelectric Coefficient

The "dE" form of the electrocaloric equation is

$$dT = -(T/\rho c_E)(\partial P/\partial T)_E \, dE, \qquad (4)$$

and it has been shown that the pyroelectric effect and the electrocaloric effect are manifestations of the same crystalline properties.[1] The pyroelectric coefficient at constant field and stress $p^{X,E}$ (hereafter written p^E because the stresses here are negligible) is by definition and from Eq. 4 given by

$$p^E = (\partial P/\partial T)_E = -(\rho c_E/T) \, \Delta T/\Delta E \qquad (4')$$

for small electrocaloric temperature changes ΔT. The variation of the pyroelectric coefficient with temperature was determined from measured values of the electrocaloric effect as suggested by Eq. (4'). The results are shown in Fig. 12. Values of c_E were obtained from Hoshino, et al.[4] Above the Curie point, the electrocaloric temperature rise is parabolic with respect to the field (see Fig. 1) so that differential values of $\Delta T/\Delta E$ (or p^E) near a particular value of field E is twice the average value for the full field step from 0 to E. Below the Curie point, on the other hand, the electrocaloric temperature rise is approximately linear with respect to field so that the differential and average values of $\Delta T/\Delta E$ (and p^E) are approximately equal. Consequently, the sensitivity of a TGS pyroelectric radiation detector could be adjusted at will by changing the biasing field if the detector is operated above the Curie temperature, whereas the sensitivity of such a detector is nearly independent of the field if it is
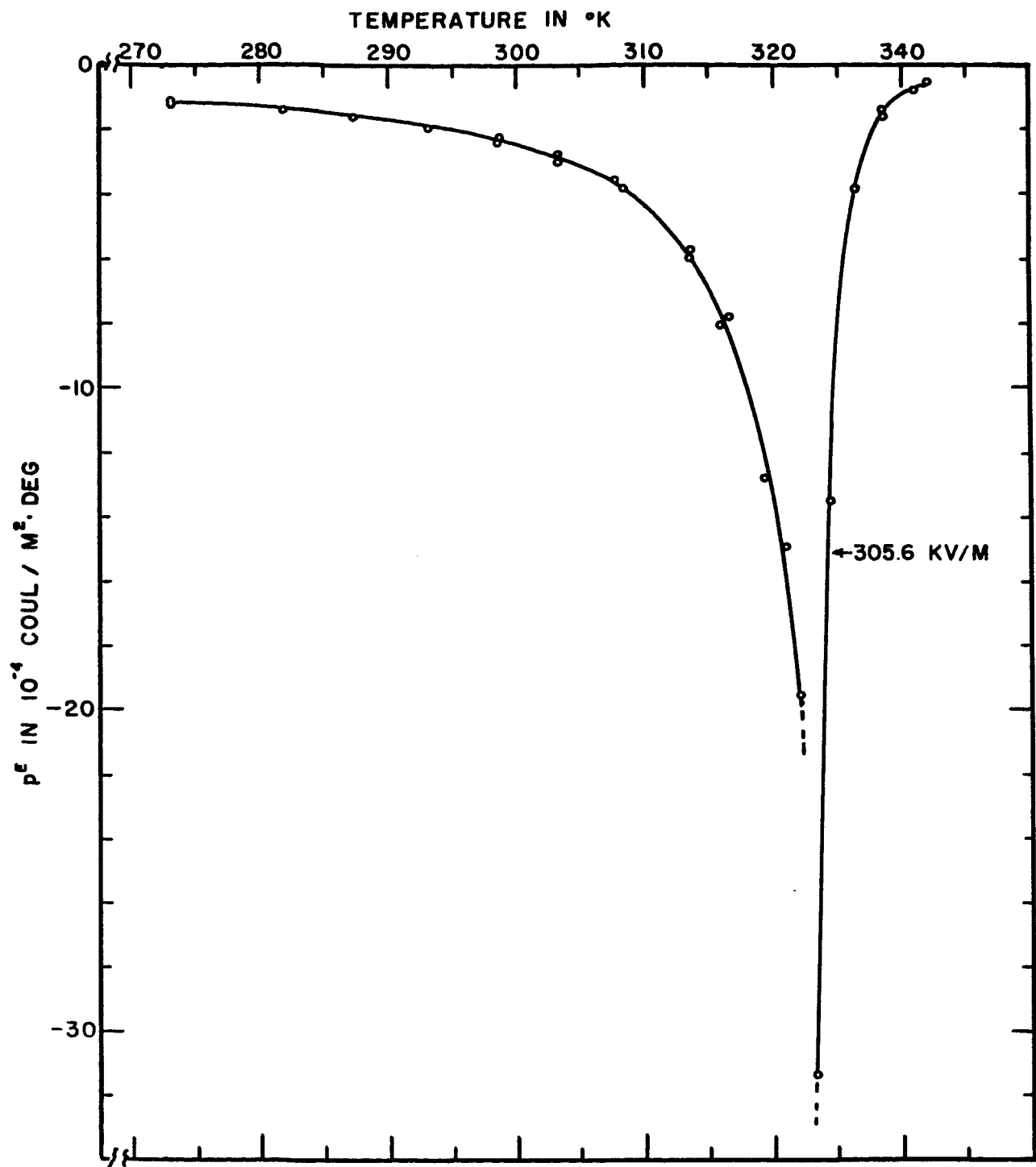
FIG. 12. PYROELECTRIC COEFFICIENT OF TGS FROM ELECTROCALORIC DATA

operated below its Curie temperature.

SUMMARY

Electrocaloric measurements of triglycine sulfate were made from 273°K to 334°K at fields up to 306 kilovolts per meter.

Relaxation polarization, ohmic leakage, and asymmetry in the polarization (which persists even after temporary heating above the Curie temperature) make accurate interpretation of the polarization measurements difficult. Moreover, the electrical properties of triglycine sulfate change with its electrical and thermal treatment during the measurements.

Nevertheless, the observed electrocaloric measurements in TGS are in accord with the Devonshire theory and yield values of 322.6°K (49.45°C) for the Curie temperature and 4280°K for the Curie constant C. Both the electrocaloric and dielectric observations confirm the accepted belief that the ferroelectric transition in TGS is of second order. The first Devonshire coefficient ω is continous with no change in slope right through the Curie temperature, $\partial\omega/\partial T$ being constant down to about 312°K where it begins to diminish significantly.

Relaxation effects prevented an accurate determination of the second Devonshire coefficient ξ. The electrocaloric data gave an indication that ξ is temperature dependent.

Values for the pyroelectric coefficient p^E were determined

from the electrocaloric measurements for the entire temperature range. Above the Curie temperature, the pyroelectric coefficient can be controlled by changing the biasing field; below the Curie temperature the pyroelectric coefficient is independent of field.

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