Ferroelectric Behavior of Triglycine Fluoberillate near T_c

Aurelio Mercado and Julio A. Gonzalo

Nuclear Science Division, Puerto Rico Nuclear Center, * *and Department of Physics, University of Puerto Rico, Mayaguez, Puerto Rico 00708*

Dielectric-constant and hysteresis-loop measurements have been performed on single crystals of triglycine fluoberillate (TGFB) in the vicinity of the critical point to characterize the second-order transition and to compare the results with previous data on its isomorph triglycine sulfate (TGS). The mean-field critical exponents and the mean-field equation of state are shown to give a good description of the ferroelectric behavior of TGFB as expected. The parameters entering in the statistical dipolar theory of ferroelectrics are derived, in some cases independently, from the dielectric-constant and hysteresis-loop measurements, allowing a distinction between dipolar and atomic (mainly ionic) polarization. The numerical values of parameters obtained in this way for TGFB, as well as for TGS, are discussed.

I. INTRODUCTION

The static ferroelectric properties of triglycine sulfate (TGS), a typical order-disorder ferroelectric, have been studied in detail[1,2] near the critical temperature. The agreement of the experimental critical exponents with the predictions of the classical mean-field theory has been shown to be quite satisfactory. Furthermore, an appropriate power-series expansion of the simple equation of state deduced within the framework of the statistical dipolar theory of ferroelectrics (equivalent to the Weiss molecular-field theory of magnetism) has been shown to yield a good description of the assymptotic temperature behavior near the critical point, both above and below the transition.

An investigation of other cases of order-disorder ferroelectric transitions was considered of interest; first to check further the validity of the mean-field theory and second to explore the possibility of extracting more information from the experimental data, in particular, regarding the separation of the strictly dipolar and the atomic (ionic and electronic) contributions to the polarization. The relative importance of the ionic and electronic contribution was discussed many years ago by Devonshire,[3] Slater,[4] and Mason,[5] in connection with other ferroelectric systems, such as barium titanate, which being a first-order transition, is more difficult to interpret than second-order transitions. We decided to study triglycine fluoberillate (TGFB), an isomorph of TGS because the crystallographic similarity to TGS allows meaningful comparison of the respective mean-field parameters. In both cases the transition goes from monoclinic space group $P2_1$, below T_c, to $P2_1/m$ above. The unit-cell parameters are almost identical giving a unit-cell volume of $v_c = 646.2$ Å^3 for TGFB to be contrasted with $v_c = 676.9$ Å^3 for TGS. The density is 1.71 and 1.69 g/cm^3, respectively. The slightly smaller volume for TGFB may be indicative of stronger interaction between dipoles, justifying, at least in part, the increase of the transition temperature which is $T_c = 346.2$ °K for TGFB, compared with 322.5 °K for TGS. On the other hand, the Curie constant values are reversed, being $C = 3560$ and $C = 2630$, respectively, for TGFB and TGS.

II. EXPERIMENTAL

The samples were plates of about $1 \times 1 \times 0.1$ cm with the main surfaces perpendicular to the ferroelectric b axis. They were cut by the wet-thread method from single crystals grown from aqueous solutions. While the optical quality of the crystals was reasonably good and the peak values obtained in dielectric-constant measurements were high, the over-all quality of the samples was inferior to that of the crystals used in the TGS investigation.[1] The details of the experimental technique for capacitance and hysteresis-loop measurements as a function of temperature have been described in previous communications.[1] In the capacitance measurements, to determine the dielectric constant, an extra precaution was taken to ensure that the parallel capacitance from the electrode leads and sample holder was accurately determined. Five samples ranging in thickness between 0.02 and 0.20 cm were measured at room temperature. From the linear plot of capacitance versus thickness for these five cases, the parallel capacitance, to be substracted from the total measured capacitance, was determined. Also the frequency dependence of the dielectric constant was checked between 10^2 and 5×10^5 Hz. Some relaxation (probably domain-wall relaxation, at the low ac amplitude of about 10 V/cm employed) was observable at room temperature and $T < T_c$ between 10^2 and 10^4 Hz, but it was not very important at 10^3 Hz, the frequency used in the series of

capacitance measurements as a function of temperature. Between 10^5 and 2.5×10^5 Hz, a series of piezoelectric resonances were clearly observed.

In order to be sure that true saturation behavior was observed in the hysteresis-loop measurements, several photographs were taken at various fixed temperatures with increasing applied voltages to the samples. Figure 1 shows a plot of the *apparent* spontaneous polarization as a function of voltage amplitude (maximum electric field per cycle). It can be observed that at temperatures close to the transition temperature saturation has been practically achieved at maximum fields of the order of 2.5 kV/cm (sample thickness ~0.1 cm). Field amplitudes of 4 kV/cm were employed, approximately twice as large as necessary for saturation in the final series of measurements. Since previous hysteresis-loop results for TGS were obtained using low fields,[1] we studied also the amplitude dependence in TGS samples. The

results were similar except that saturation at T close to T_c was achieved at much lower fields (~0.6 kV/cm) due to the smaller coercive field, and probably, to the higher quality of the samples. To be able to compare with present results for TGFB, a new series of measurements were performed for TGS, using an amplitude of 1 kV/cm, larger by a factor of 4 than that used in some of the previous work. It may be noted that using large fields seems to produce a slight distortion of the hysteresis loops (departure from rectangularity), which is more apparent at $T \simeq T_c$. This is the reason for avoiding large fields in some of the previous investigations. However, in order to make meaningful comparisons of the coefficients, absolute values for the polarization are needed. Therefore, it was decided to use high fields. The "scaling" behavior reported in Ref. 1 is fulfilled by data obtained with high-field amplitudes as well as with lower-field amplitudes, changing only the
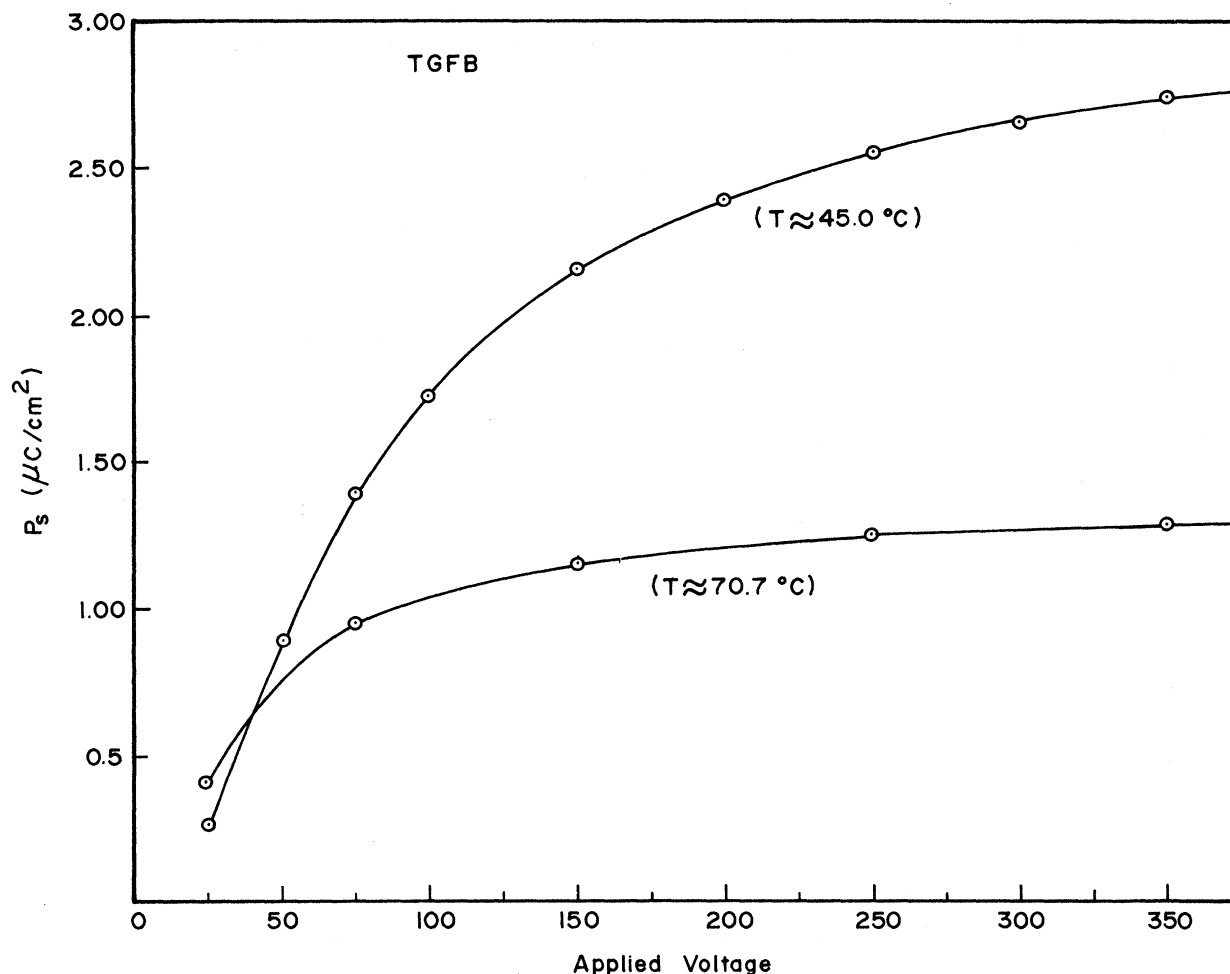

FIG. 1. Apparent spontaneous polarization as a function of applied voltage for TGFB. The crystal thickness was 0.098 cm.

scale factors.

III. RESULTS

The dielectric-constant measurements as a function of temperature gave a sharp peak at $T_c = (73.30 \pm 0.05)$ °C. Several samples were examined and the scattering of transition temperatures was within 0.20 °C. Figure 2 gives a plot of ϵ^{-1} vs ΔT. The Curie constant determined from this plot was $C^+ = 2630$ and the ratio of slopes above and below T_c was $C^+/C^- \simeq 2.37$. The departure from the classical (mean-field) value $C^+/C^- = 2$, can be accounted for considering the deviations from true "isothermal" behavior[1] at the frequency of these measuremenst (10^3 Hz). The remaining dielectric constant in the paraelectric region at $T \gg T_c$ determined from

$$\epsilon_{obs} = \epsilon_0 + C^+/(T_c - T) \qquad (1)$$

gave a relatively large value $\epsilon_0 = 110$. The corresponding observed values using TGS samples were $C^+ = 3560$, $C^+/C^- \simeq 2.42$, and $\epsilon_0 = 65$.

Hysteresis-loop measurements in the vicinity of T_c gave the following results for TGFB

samples:

$$P_s = (A \Delta T)^\beta, \qquad \text{with } \beta = 0.49 \pm 0.02$$

$$A = 0.760 \ (\mu C/cm^2)^2/°C \ , \qquad (2)$$

$$P = (B \Delta E)^{1/\delta} \ , \quad \text{with } 1/\delta = 0.36 \pm 0.03$$

$$B = 2.20 \times 10^{-4} \ (\mu C/cm^2)^3/(V/cm) \ , \qquad (3)$$

where P_s is the spontaneous polarization and P the polarization as a function of field. It was concluded that up to temperatures for which $\Delta T/T_c \simeq 2 \times 10^{-4}$ the classical exponents $\beta = \frac{1}{2}$ and $\delta = 3$ are valid as in the case of TGS. The transition temperature as determined from a linear plot P_s^2 vs T was $T_c = (73.30 \pm 0.05)$ °C for the same sample used in the dielectric-constant measurements, in excellent agreement with the peak temperature of those measurements. The value for the coefficient β was obtained by interpolating between the values determined from hysteresis loops closest to T_c (from above and from below). Since the coefficients A and B for TGS previously published[1] referred to "unsaturated" hysteresis loops, as discussed in the Sec. II, we report here the values
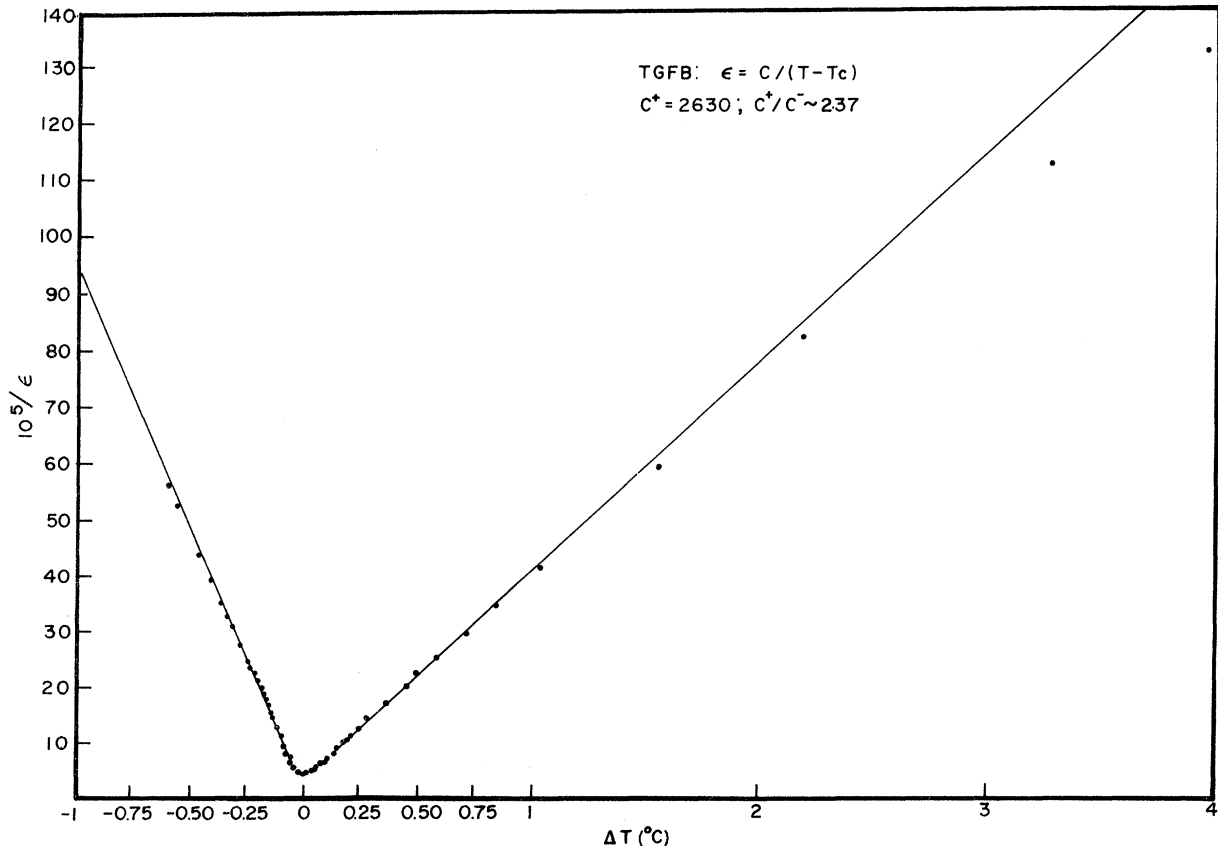

TGFB: $\epsilon = C/(T-Tc)$
$C^+ = 2630$; $C^+/C^- \sim 2.37$

FIG. 2. Inverse dielectric constant of TGFB as a function of temperature in the vicinity of T_c.

obtained from saturated loops:

$$A = 0.425 \ (\mu C/cm^2)^2/^\circ C,$$

$$B = 2.09 \times 10^{-4} \ (\mu C/cm^2)^3/(V/cm) \ .$$

In Fig. 3 a plot of the hysteresis-loop results for TGFB is given in terms of the "scaled variables" $P/(\Delta T)^{1/2}$ vs $E/(\Delta T)^{3/2}$. The data for various temperatures below T_c, ranging from $\Delta T = T - T_c = -0.667\ ^\circ C$ to $\Delta T = -0.060\ ^\circ C$, scale into one branch of the curve, while the data for T above T_c, from $\Delta T = 0.013\ ^\circ C$ to $\Delta T = 0.350\ ^\circ C$, scale into another branch, in the same fashion as was observed previously for TGS. The data are shown to fit the mean-field curves

$$\frac{\lambda_1 E}{|\Delta T|^{3/2}} = \frac{\lambda_2 P}{|\Delta T|^{1/2}} \left(\frac{1}{3} \frac{(\lambda_2 P)^2}{|\Delta T|} \mp 1 \right) , \tag{4}$$

where the (-) sign applies for $T < T_c$ and the (+) sign for $T > T_c$. The asymptotic behavior for E large and $T \gtrless T_c$ is given by

$$E = \tfrac{1}{3} \lambda_1^{-1} (\lambda_2 P)^3$$
or
$$P = [(3\lambda_1/\lambda_2^3) E]^{1/3} = (BE)^{1/3} , \tag{5}$$

and the asymptotic behavior for E small and $T < T_c$ by

$$\tfrac{1}{3} (\lambda_2 P_s)^2/\Delta T = 1$$
or
$$P_s = [(3\lambda_2^{-2}) \Delta T]^{1/2} = (A \Delta T)^{1/2} \ . \tag{6}$$

From this one can calculate $\lambda_2 = (3/A)^{1/2}$ and $\lambda_1 = \tfrac{1}{3} (3/A)^{3/2} B$, in terms of the experimental coefficients A and B. Normalized variables P/P_0 and E/E_0 have not been used as previously because the choice of parameters from low-temperature data is rather arbitrary if one is going to analyze data for the critical region only. The theoretical curves shown in Fig. 3 are chosen to best fit all experimental points, rather than the asymptotic behavior, but the resulting coefficients come out approximately the same.

IV. DISCUSSIONS AND CONCLUSIONS

For order-disorder ferroelectrics the statistical dipolar theory of ferroelectrics, analogous to the Weiss molecular-field model in magnetism, seems to be a simple and fruitful approach. The equation of state[6] can be expressed as follows:

$$P_d/N\mu = \tanh(F\mu/kT) , \tag{7}$$

where P_d is the dipolar polarization, $N\mu$ is the saturation dipolar polarization (N is the number of unit dipoles per unit volume and μ is the unit dipole moment), F is the internal field seen by the dipoles, and kT the thermal energy. If one distinguishes between *atomic* (electronic and ionic) polarization, which should be, up to certain limits,

approximately linear with internal field, and *dipolar* polarization, which is not, one can write

$$F = E + \beta P_a + \beta P_d = E + \beta(\gamma F) + \beta P_d , \tag{8}$$

where β is related to the generalized Lorentz factor which depends on the crystal structure and γ is the combined electronic and ionic polarizability per unit volume. From Eq. (8) the internal field can be derived as

$$F = (E + \beta P_d)/(1 - \beta\gamma) \ . \tag{9}$$

The experimentally observable polarization would be

$$P = P_a + P_d = \left(\frac{\gamma}{1 - \beta\gamma} \right) E + \left(\frac{\beta\gamma}{1 - \beta\gamma} + 1 \right) P_d \ . \tag{10}$$

For $T < T_c$ the second term in Eq. (10) predominates even at temperatures very close to T_c and for external fields relatively high. For $T > T_c$ the second term dominates. Only the first term remains at $T \gg T_c$, where the residual dielectric constant would be

$$\epsilon_0 = 1 + 4\pi\gamma/(1 - \beta\gamma), \quad \epsilon_0 \equiv \epsilon(T) - C/(T - T_c) \ . \tag{11}$$

Let us consider the equation of state in the vicinity of the transition temperature. Since Eq. (10) gives the experimental polarization in terms of P_d, we have

$$P_d \simeq (1 - \beta\gamma) P = \kappa P; \quad \kappa \equiv (1 - \beta\gamma) \ . \tag{12}$$

Then Eq. (7) becomes

$$\frac{\kappa P}{N\mu} = \tanh\left(\kappa \frac{E + \beta P}{\beta N\mu} \frac{T_c}{T} \right), \quad T_c = \frac{\beta N\mu^2/\kappa^2}{k} , \tag{13}$$

or putting E explicitly in terms of P only,

$$E = \frac{\beta N\mu}{\kappa} \left[\frac{T}{T_c} \tanh^{-1}\left(\frac{\kappa P}{N\mu} \right) - \frac{\kappa P}{N\mu} \right] \ . \tag{14}$$

The derivative dE/dT which is proportional to the inverse dielectric constant, for $T > T_c$ and E small ($\kappa P \ll N\mu$), can be shown to be

$$\frac{dE}{dt} \equiv 4\pi \frac{T - T_c}{C} = \beta\left(\frac{T - T_c}{T_c} \right) \ . \tag{15}$$

On the other hand, the asymptotic behavior of P for T to T_c can be also obtained from Eq. (14):

$$T < T_c, \quad E \ll \beta P \rightarrow (\kappa P_s/N\mu)^2 = 3(\Delta T/T_c) \tag{16}$$
and
$$T \gtrless T_c, \quad E \gg \beta P \rightarrow (\kappa P/N\mu)^3 = 3(\kappa E/\beta N\mu) \ . \tag{17}$$

Now we can compute various mean-field parameters from data obtained from dielectric-constant and hysteresis-loop measurements. β can be calculated from dielectric-constant data only, by means of Eqs. (13) and (15):
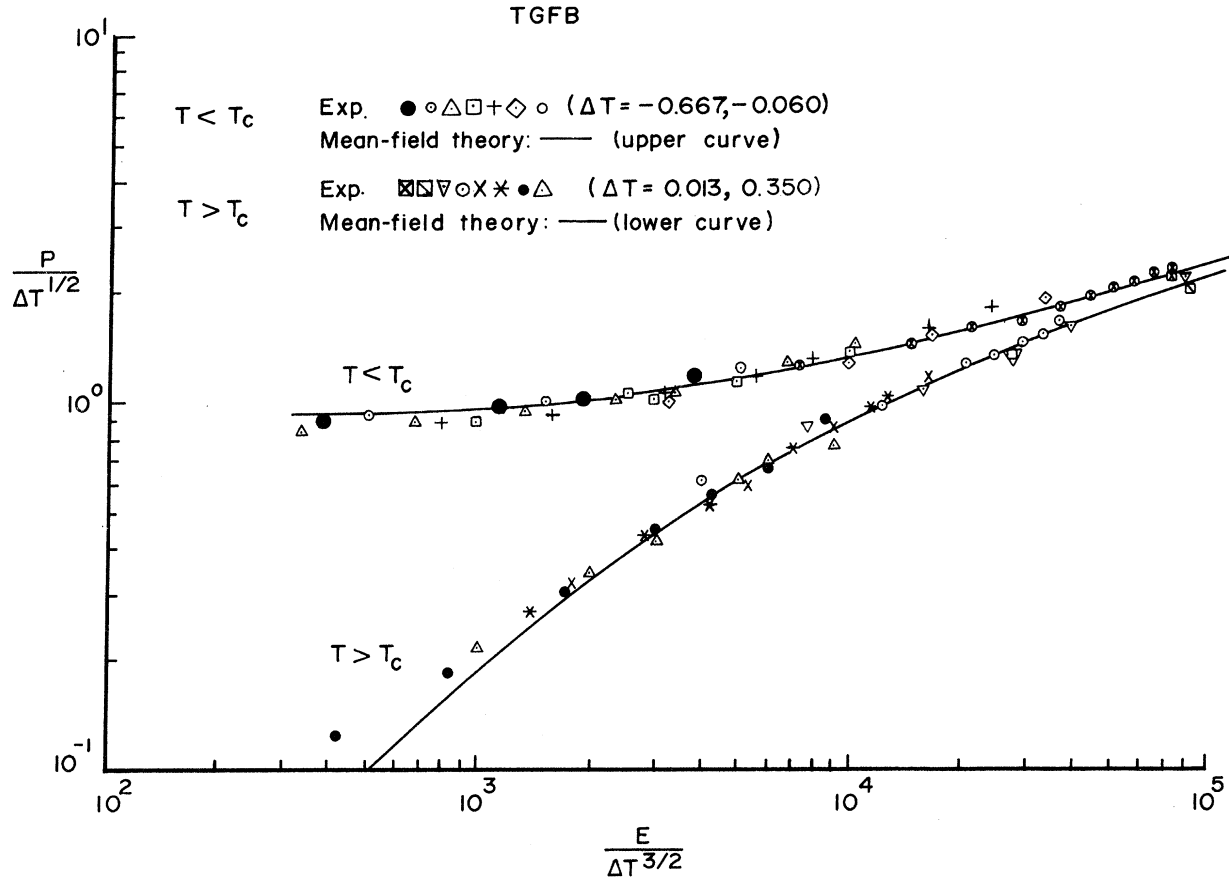
TGFB

FIG. 3. Log-log plot of $P/\Delta T^{1/2}$ vs $E/\Delta T^{3/2}$ for TGFB in the vicinity of T_c. Experimental points marked by the same symbol correspond to the same value of ΔT below and above T_c. The sequence is $\Delta T = -0.667$, -0.557, -9.458, -0.357, -0.259, -0.160, -0.060 °C (below T_c) and $\Delta T = 0.013$, 0.039, 0.090, 0.139, 0.239, 0.279, 0.391, 0.350 °C (above T_c).

$$\beta = 4\pi T_c/C \quad . \tag{18}$$

Alternatively, from hysteresis loops $(T \lessgtr T_c)$ only, by means of Eqs. (16) and (17):

$$\beta = (P_s^2 E/P^3 \Delta T) T_c \quad . \tag{19}$$

The other parameters can be calculated as follows: From hysteresis-loop data only,

$$N = \beta P_s^2/k\Delta T \quad , \tag{20}$$

using Eqs. (13) and (16); from dielectric constant alone

$$\gamma = (1/\beta)(\epsilon_0 - 1)/[4\pi + \beta(\epsilon_0 - 1)] \quad , \tag{21}$$

using Eq. (11) (note that this expression is equivalent to the Clausius–Mossotti relation); and from a combination of both

$$\mu^2 = [(1 - \beta\gamma)^2/N^2]\tfrac{1}{3} T_c(P_s^2/\Delta T) \quad , \tag{22}$$

from Eq. (16) in which the results from Eqs. (19)–(21) along with the experimental value for $P_s^2/\Delta T$ can be substituted.

Of course this model is a simplification in the sense that all elementary permanent dipoles are considered to have the same moment and are sensing the same mean internal field. Also we have assumed the atomic polarization to be linear with internal field. These assumptions may or may not be valid in actual ferroelectric crystals. We have computed the numerical value for TGFB and

TABLE I. Mean-field parameters for TGS and TGFB. (All numerical values are given in cgs-esu units.)

Parameter	TGS	TGFB
$\beta = 4\pi T_c/C$ $(T > T_c)$	1.14	1.65
$\beta = T_c(P_s^2/\Delta T)/(P^3/E)$ $(T < T_c)$	0.98	1.25
$N = \beta P_s^2/3k\Delta T$	0.90×10^{22}	2.07×10^{22}
$n = N v_c$	~ 6	~ 12
$\gamma = (1/\beta)(\epsilon_0 - 1)/[4\pi + \beta(\epsilon_0 - 1)]$	0.75	0.56
$\mu = N^{-1}[(1 - \beta\gamma)^2 P_s^2/3(\Delta T/T_c)]^{1/2}$	3.3×10^{-18}	0.9×10^{-18}

TGS using Eqs. (18)–(22). They are shown in Table I. It may be noted that for both crystals β seems to be slightly lower in the ferroelectric phase than in the paraelectric phase. It is conceivable that the small unit-cell distortions which accompany the transition may produce small changes in β. The number of dipoles per unit volume leads to $n = Nv_c$ (dipoles per unit cell) approximately 6 for TGS and slightly more than 12 for TGFB. These figures seem to be too high, since one would expect *two* dipoles per unit cell, corresponding to the two chemical units per unit cell. They differ by a factor of 2, which also seems unrealistic in view of the close crystallographic analogy of both systems. It may be noted, however, that for TGS[7] and TGFB,[8] the change in specific heat at the transition, which in the statistical dipolar theory is directly proportional to N, also indicates a factor of 2. In addition, the expected absolute value $\Delta C_p = \frac{3}{2} Nk$, with N given by

Eq. (20), while still somewhat too small (roughly by 50%) in comparison with the experimental data,[9] is closer to these data with $n = 6$ (TGS) and $n = 12$ (TGFB) than with $n = 2$. The difference in elementary dipole moments for TGS and TGFB also seems too large, however, the resulting moments per unit volume $N\mu$ are closer to each other than the μ, as expected.

In summary, one can conclude that, while the statistical dipolar model discussed here appears too simple to be correct, it gives a fairly good picture of the transitions for TGFB and TGS, and that the characteristic parameters determined from different experimental data are reasonably consistent with each other.

ACKNOWLEDGMENT

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

[1]J. A. Gonzalo, Phys. Rev. 144, 662 (1966); Phys. Rev. Lett. 21, 749 (1968); Phys. Rev. B 1, 3125 (1970).

[2]E. Nakamura et al., J. Phys. Soc. Jap. Suppl. 28, 271 (1970); K. Deguchi and E. Nakamura, Phys. Rev. B 5, 1072 (1972).

[3]A. F. Devonshire, Philos. Mag. 40, 1040 (1949).

[4]J. C. Slater, Phys. Rev. 78, 748 (1950).

[5]W. P. Mason, Piezoelectric Crystals and their Application to Ultrasonics (Van Nostrand, New York, 1950).

[6]See, for instance, J. A. Gonzalo and J. R. López-Alonso, J. Phys. Chem. Solids 25, 303 (1964), and references therein.

[7]B. A. Strukov, S. A. Taraskin, G. L. Skoromokhova, and K.

A. Minaeva, Bull. Acad. Sci. USSR Phys. Ser. 29, 982 (1965).

[8]B. A. Strukov, S. A. Taraskin, and V. A. Koptsik, Zh. Eksp. Teor. Fiz. 31, 1037 (1966) [Sov. Phys.-JETP 24, 692 (1967)].

[9]It may be pointed out in this connection that the more recent and accurate data by S. A. Taraskin et al. {Fiz. Tverd. Tela 12, 1386 (1970) [Sov. Phys.-Solid State 12, 1089 (1970)]} and also by M. R. Moldover (private communication) show a considerable lower value of the specific-heat jump at T_c. Some of these data suggest that the jump might be composed of a smooth logarithmic contribution (possibly due to weak fluctuation effects) and a steplike contribution, which would be the one to compare with $3Nk/2$.

Heat Capacity of Metallic V₂O₃ at High Pressure

D. B. McWhan and J. P. Remeika

Bell Laboratories, Murray Hill, New Jersey 07974

S. D. Bader,* B. B. Triplett,*† and N. E. Phillips*

Inorganic Materials Research Division of the Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California, 94720

The heat capacity of V₂O₃ has been measured between 0.3 and 10 K at pressures of 1 and 25 kbar. The results confirm that the very high electronic heat capacities measured for doped samples are characteristic of pure V₂O₃ in the metallic phase.

Vanadium sesquioxide has a metal-to-antiferromagnetic-insulator transition at 1 atm and 150–160 K. The low-temperature insulating phase can be suppressed by doping [$(V_{1-x}Ti_x)_2O_3$ with $x \approx 0.05$][1] or by changing the stoichiometry [$V_{2-x}O_3$ with $x \approx 0.03$][2] or by pressure.[3] In the first two cases,

heat-capacity studies at low temperatures on the metallic phases have revealed very large linear contributions.[1,4] These have been attributed to the highly correlated nature of a metallic state on this verge of localizing to form a Mott insulator. The heat capacity and magnetic susceptibilities[1,4] are