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CONCERNING THE THERMODYNAMICS OF THE PHASE TRANSITION IN FERROELECTRIC TRIGLYCINE FLUOROBERYLLATE

B. A. STRUKOV, S. A. TARASKIN, and V. A. KOPTSIK

Moscow State University

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The temperature dependences of the dielectric permittivity, spontaneous polarization, and specific heat of triglycine fluoroberyllate are investigated in the immediate vicinity of the Curie point. The expansion parameters for the Gibbs free energy function are determined and the parameter δ which defines the correlation energy is estimated.

INTRODUCTION

An expansion of the type

$$\Phi = \Phi_0 + A(T - T_c)P^2 + BP^4 + CP^6 + \delta(\operatorname{grad} P)^2 \quad (1)$$

is commonly used to describe the behavior of ferroelectric crystals in the vicinity of a second-order phase transition.

According to estimates of Ginzburg,[1] in ferroelectrics the correlation energy $\delta(\text{grad P})^2$ becomes of the order of the volume energy when the polarization P changes at distances which exceed the lattice constant appreciably: for $T \ll T_c$ we have $AT_c \sim \delta/l^2$, $l \gg d \sim 4 \times 10^{-8}$ cm which leads to an anomalously narrow temperature interval within which one can expect a deviation from (1) and to a negligibly small effect of the fluctuations on the temperature dependences of the spontaneous polarization, the dielectric permittivity, and the specific heat.

However, recent data on the temperature dependences of the thermodynamic parameters of ferroelectrics near the Curie point indicate that the problem concerning the role of fluctuations in ferroelectric phase transitions must be defined more accurately. The experimentally measured jump in the specific heat of the phase-transition point for triglycine fluoroberyllate (TGFB) crystals (T = 49° C) is not described by expansion (1),[2] and the specific heat itself has at the Curie point a logarithmic singularity;[3] at the same time no deviations are noted from the "normal" temperature dependences of the spontaneous polarization and the dielectric permittivity.[4, 5]

In this connection it appears justified to continue investigations of the properties of ferroelectric crystals in the immediate vicinity of the point of a second-order phase transition. In this paper we present data of an experimental investigation of the electrical and thermal properties of the ferroelectric crystal triglycine fluoroberyllate in the vicinity of the Curie point which occurs according to the data of [6, 7] in the region of 70° C; the spontaneous polarization appears along the twofold axis.

EXPERIMENTAL RESULTS

The temperature dependences of the dielectric permittivity along the polar axis ϵ_p, of the spontaneous polarization P_s, and of the specific heat at constant pressure and electric field $c_{p,E}$ were measured on a sample placed in a vacuum adiabatic calorimeter of the construction of Strel'kov et al.[2, 8] The values of ϵ_p and P_s were determined under conditions of zero temperature change of the calorimeter; the accuracy of the temperature measurement was of the order of 5×10^{-4}° C. On going from one temperature to the next the capacitor plates were shorted out (E = 0) and a measured amount of heat was supplied to the sample. The ratio of this amount of heat to the equilibrium temperature change determined the specific heat of the crystal $c_{p,E} = \Delta Q/\Delta T$. Thus the measurement of all three quantities ϵ_p, P_s, and $c_{p,E}$ was carried out on the same crystal under identical conditions.

In measuring ϵ_p, 10 millivolts were applied to the sample; this voltage produced within the sample a field of the order of 0.03 V/cm which can be considered very small. The dielectric permittivity was measured at a frequency of 20 kcs with the aid of a precise logarithmic Sullivan-type bridge with an accuracy of 0.1%.

To determine the spontaneous polarization, we used a static method consisting in measuring the electrical charge remaining on a large (~ 10 μF) mica capacitance C_0 connected to the crystal in series. The spontaneous polarization

$$P_s = (e_+ + e_-)/2S,$$

where e_+ and e_- are the charges on C_0 for different polarizations of the applied voltage and S is the area of the electrodes deposited on the sample surfaces perpendicular to the axis of spontaneous polarization. It should be noted that this method is applicable only after prolonged annealing of the crystal at ~ 100° C which removes the natural unipolarity of the sample; after annealing a single-domain state of arbitrary sign is retained for a long time after removing the electric field, even in the immediate vicinity of the Curie point. Use of the electronic "Orion" equipment to measure the charge made it possible to attain an accuracy of 3 per cent in the value of P_s.

1. THE DIELECTRIC PERMITTIVITY

Figure 1 shows the temperature dependence of the reciprocal of the dielectric permittivity $1/\epsilon_p$ of a TGFB crystal. The dependence of $\epsilon_p^{-1}(T)$ on both sides of the transition point is, in the first approximation, linear, the ratio of the slopes being

$$\frac{d}{dT}\left(\frac{1}{\varepsilon_p}\right)_{T<T_c} \Big/ \frac{d}{dT}\left(\frac{1}{\varepsilon_p}\right)_{T>T_c} = 3{,}4.$$

The Curie point obtained from the maximum value of the dielectric permittivity is at room temperature $T_c^\epsilon = 72.85 \pm 0.05$° C. In the paraelectric phase the dependence of $1/\epsilon_p$ on T is well described by the equation

$$4\pi/\varepsilon_p = 2A(T - T_c'), \tag{2}$$

which follows from expansion (1) with $A = 1.72 \times 10^{-3}$ deg^{-1}. T_c' in (2) is obtained by extrapolating the dependence $\epsilon_p^{-1}(T)$ to $\epsilon_p^{-1} = 0$.

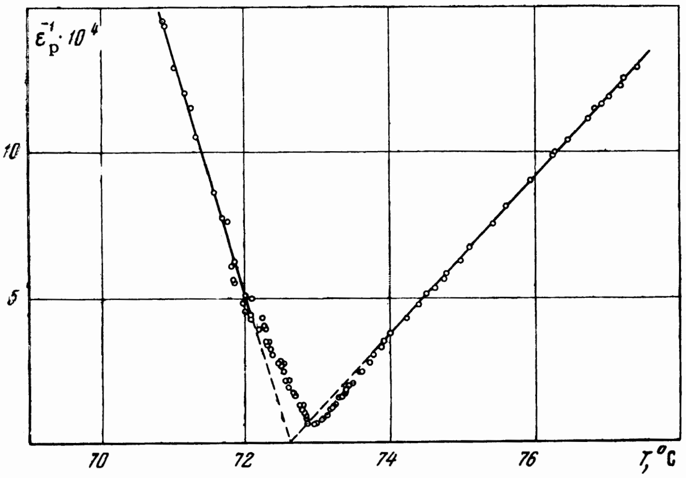

FIG. 1. Temperature dependence of the reciprocal of the dielectric permittivity $1/\epsilon_p$ of a TGFB crystal (dashed line—assumed variation of $1/\epsilon_p$).

As can be seen from Fig. 1, a deviation from linearity is noted near the Curie point both in the paraelectric and in the ferroelectric phase. For $T > T_c^\epsilon$ the increase in the dielectric permittivity is somewhat more rapid than one would expect from (2); in the polar phase a break is noted in the $\epsilon_p^{-1}(T)$ dependence at a temperature $T \cong 72$° C. The reasons for the observed deviations will be discussed below.

2. SPONTANEOUS POLARIZATION

Figure 2 illustrates the temperature dependence of the spontaneous polarization of a TGFB crystal in the ferroelectric phase. The spontaneous polarization vanishes at a temperature T_c^ϵ. The $P_s^2(T)$ dependence is well described by an equation which follows from (1) for the spatially homogeneous case:

$$P_s^2 = -\frac{A(T-T_c)}{2B} - \frac{3}{8}\frac{A^2C}{B^3}(T-T_c)^2, \tag{3}$$

where the values of the coefficients B and C, determined from a least-squares treatment of the dependence $P_s(T)$ are: $B = 0.61 \times 10^{-10}$, and $C = 0.98 \times 10^{-19}$ cgs esu.

For comparison we show on Fig. 2 also the temperature dependences of P_s^2 obtained experimentally and calculated from (3) with the above values of the coefficients A, B, and C. In the temperature range from T_c^ϵ to $T_c^\epsilon - 3$° C the square of the

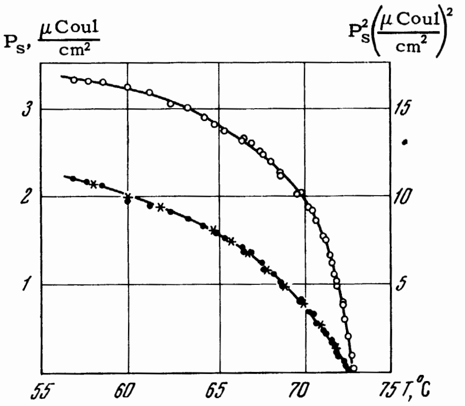

FIG. 2. Temperature dependence of the spontaneous polarization of a TGFB crystal: ○—temperature dependence of the spontaneous polarization of a TGFB crystal, ●—temperature dependence of P_s^2, *—points corresponding to Eq. (3).

spontaneous polarization is a linear function of the temperature.

3. SPECIFIC HEAT

The general form of the specific-heat anomaly in the TGFB crystal for $E = 0$ is shown in Fig. 3. As in the case of the previously investigated triglycinesulfate,[2] the increase in the specific heat splits into three regions: 44–54, 54–62, and 62–72° C. In the region of the phase transition the specific heat increases particularly rapidly, reaching at a temperature of $T_c^c = 72.0 \pm 0.1$° C a maximum value of ~ 0.66 cal/g-deg. This temperature corresponds to the break in the $\epsilon_p^{-1}(T)$ dependence noted above. The difference between the temperatures T_c^ϵ and T_c^c which has also been observed in triglycinesulfate[9] amounts here to 0.85 ± 0.15° C. It is curious to note that the decrease in the specific heat above T_c^c takes place as it were in two stages: the first stage in the range T_c^c to T_c^ϵ, and the second stage in the range T_c^ϵ to $T_c^c + 2$° C.

Figure 4 shows the dependence of the specific heat $c_{p,E}(T)$ in the region where it has its maximum, the points corresponding to heating intervals of ~ 0.07° C. At the temperature corresponding to the appearance of spontaneous polarization in the crystal, its specific heat experiences a jump which goes over continuously into a maximum shifted to the left. The theoretical variation of the specific heat which can be calculated from (3)

$$\Delta c_{p,E} = ATdP_s^2/dT, \qquad (4)$$

coincides approximately in its value to the "bulge" in the variation of the specific heat for $T > T_c^c$.

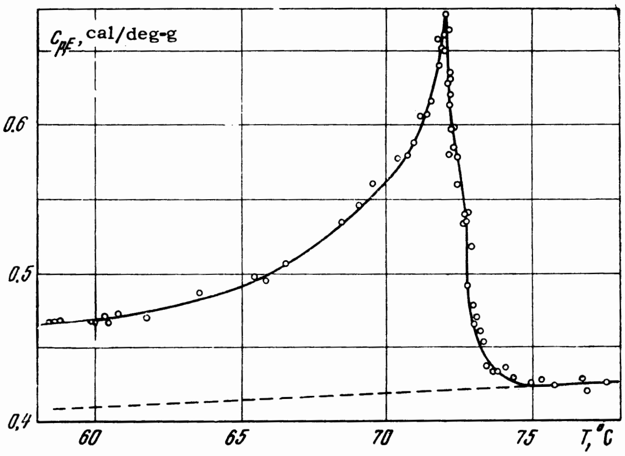

FIG. 4. Temperature dependence of the specific heat of a TGFB crystal in the region of the phase transition (dashed line—the same as in Fig. 3).

DISCUSSION OF THE RESULTS

In comparing the obtained results with the theory one must bear in mind that the deviations of the experimental dependences from the theoretical ones [relations (1)–(4)] can be due not only to fluctuation effects but also to the inevitable imperfection of the crystal samples (point defects, impurities, dislocations). Since it is difficult to control these types of imperfections, we shall bear in mind that a decrease in the quality of the crystal leads, as a rule, to a "washing out" of anomalies, the appearance of "tails" of the spontaneous polarization, and to a decrease in the value of ϵ_{max}. In our case the imperfection of the crystal expressed itself above all in the fact that the temperatures T_c and T_c^c did not coincide and in the appearance of a "bulge" on the decreasing branch of the specific heat. A similar situation was observed previously in measurements at the critical point[10] and in the ferromagnetic phase transition in gadolinium.[11] The break in the $\epsilon_p^{-1}(T)$ dependence in the ferroelectric phase is apparently due to the same reason.

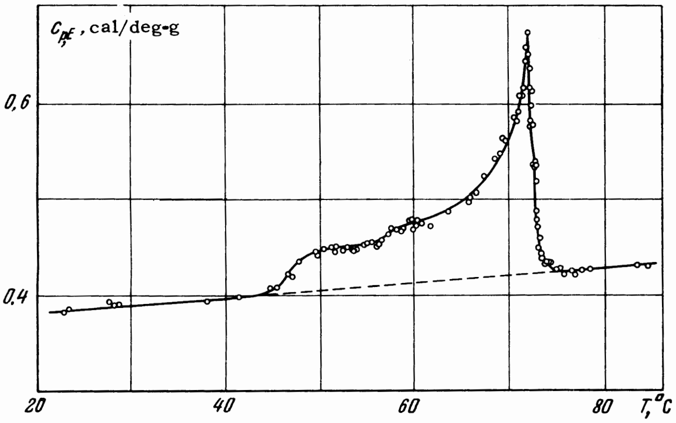

FIG. 3. The general form of the specific heat anomaly of a TGFB crystal [dashed line—tangent of the normal course of C(T)].

On the other hand, the change in the Curie constant in the paraelectric phase near T cannot be ascribed to the effect of defects since the latter could only decrease ϵ_p and not increase it; this is borne out by the numerous experiments on the effects of radioactive irradiation on the properties of ferroelectrics. In the temperature region where the deviation in the $\epsilon_p^{-1}(T)$ dependence from linearity starts there appears in the paraelectric phase additional heat capacity which may be connected with fluctuation effects (disturbance of the short-range order).

A plot on a semilogarithmic scale made it possible to interpolate the specific-heat "tail" in this temperature range (T_c^ϵ to $T_c^\epsilon + 2$° C) using the equation

$$\Delta c_{p,E} = -A \ln|T - T_c^{\varepsilon}| + B, \tag{5}$$

where the values of the coefficients turned out to be: A = 16.5 cal/mole-deg, B = 6.2 cal/mole-deg (a quantitative processing of the values of the specific heat in the ferroelectric phase turned out to be impossible because of the indeterminacy in the choice of the temperature at the origin). The value of the coefficient A turned out to be the same in order of magnitude as the corresponding value for the triglycine sulfate crystal.[3]

We attempted to estimate the coefficient δ in expansion (1) by comparing (5) with Levanyuk's formula for the specific heat of the paraelectric phase:[12]

$$\Delta c_p = \frac{kT^2A^2}{8\pi^2\delta^{3/2}} \ln|T - T_c|$$

[here A is the coefficient in the expansion (1)]. Such a comparison yields $\delta \sim 10^{-16}$ cm^2, whence we have for the characteristic length $l^2 = \delta/AT_c \sim 1.6 \cdot 10^{-16}$ cm^2, i.e., $\sim d^2$. It is interesting to note that Ginzburg's estimates in [1] for BaTiO$_3$ crystals were also based on the value $\delta \sim 10^{-16}$ cm^2; the large value of l^2 was then obtained on account of the smallness of the product AT_c which $\sim 1.5 \times 10^{-2}$ for BaTiO$_3$ but ~ 0.5 for TGFB crystals. The small value of l obtained leads to definitely incorrect results in estimates of the temperature interval of the applicability of the phenomenological theory according to Ginzburg's formula:[1]

$$\frac{T - T_c}{T_c} \gg \frac{\varkappa^2 T_c B^2}{8\pi^2\delta^3 A} \sim 0.2, \tag{6}$$

i.e., $T - T_c \gg 50°$ C!

It should however be noted that inequality (6) is applicable only to the case of non-uniaxial ferroelectrics when the average value of the square of the Fourier component of the polarization fluctuation does not depend on the direction of the wave vector. In ferroelectrics with a single polar axis it turns out that $\overline{|P_{kz}|^2}$ depends on the angle ϑ between the direction of this axis and the **k** vector:[12]

$$\overline{|P_{kz}|^2} = \frac{\varkappa T}{2\left(\tfrac{1}{2}A(T - T_c) + 2\pi\cos^2\theta + \delta k^2\right)V},$$

and the condition for the temperature interval in which the fluctuations are relatively small:

$$\frac{A(T - T_c)}{2B} \gg \sum_k \overline{|P_{kz}|^2},$$

reduces to

$$\frac{T - T_c}{T_c} \gg \exp\left\{-\frac{8\pi\sqrt{2\pi}\,\delta^{3/2}}{B\varkappa T}\right\} \sim e^{-20}.$$

There are thus good reasons for assuming that the thermodynamic theory of ferroelectricity based on expansion (1), should for uniaxial crystals have a region of applicability which excludes only a small neighborhood of the Curie point of the order of 0.01–0.1° C. The experimental data available at present confirm this in general. For a more complete comparison of theory and experiment one must investigate more carefully the effect of crystal imperfection on the behavior of its thermodynamic parameters near the Curie point.

In conclusion we consider it our pleasant duty to express our deep gratitude to B. Brzhezina (Physics Institute, Academy of Sciences, Chuvash S.S.R.) who supplied the TGFB crystal for our investigations, A. P. Levanyuk for valuable advice in the course of the discussion of the results, and also V. G. Vaks and A. I. Larkin for useful discussions.

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[1] V. L. Ginzburg, FTT **2**, 2031 (1960), Soviet Phys. Solid State **2**, 1824 (1960).

[2] B. A. Strukov, FTT **6**, 2862 (1964), Soviet Phys. Solid State **6**, 2278 (1965).

[3] J. Grindlay, Phys. Letters **18**, 239 (1965).

[4] S. Triebwasser, IBM J. Res. and Develop. **2**, 212 (1959).

[5] B. A. Strukov, Phys. Stat. Sol. **14**, K135 (1966).

[6] S. Hoshino, T. Mitsui, F. Iona, and R. Pepinsky, Phys. Rev. **107**, 1255 (1957).

[7] A. S. Sonin, I. S. Rez, V. V. Gladkiĭ, and A. A. Filimonov, Voprosy Radioelektroniki, ser. III, No. 4, 86 (1961).

[8] P. G. Strelkov, E. S. Itskevich, V. N. Kostryukov, G. G. Mirskaya, and B. N. Samoĭlov, ZhFKh **28**, 459 (1954).

[9] B. A. Strukov, S. A. Taraskin, G. L. Skoro mokhova, and K. A. Minaeva, Izv. AN SSSR, ser. fiz. **29**, 982 (1965), transl., Bull. Acad. Sci. Phys. Ser. p. 982.

[10] Yu. R. Chashkin, V. G. Gorbunova, and A. V. Voronel', JETP **49**, 433 (1965), Soviet Phys. JETP **22**, 304 (1966).

[11] A. V. Voronel', S. R. Garber, A. N. Simkina, I. A. Charkina, JETP **49**, 429 (1965), Soviet Phys. JETP **22**, 301 (1966).

[12] A. P. Levanyuk, Izv. AN SSSR ser. fiz. **29**, 879 (1965), transl., Bull. Acad. Sci. Phys. Ser. p. 885.

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