

Singularity of the free energy of the ferroelectrics triglycine sulfate and triglycine selenate

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(Received 9 January 1990; revised manuscript received 30 May 1990)

The susceptibility scaling function for the ferroelectrics triglycine sulfate (TGS) and triglycine selenate (TGSe) was studied in the paraelectric phase. It was shown that neither mean-field theory nor the approximate model derived from the Larkin-Khmelnitsky theory accurately described the paraelectric-ferroelectric phase transition. Arguments are presented to support the thesis that the critical properties of TGS and TGSe cannot be described based on an analytical form of the free energy.

INTRODUCTION

Crystals of triglycine sulfate (TGS) and triglycine selenate (TGSe) are among the ferroelectrics hitherto most frequently tested. The majority of the experimental results obtained up to now for TGS (e.g., Refs. 1 and 2) have been interpreted, as for many other ferroelectrics, based on the mean-field theory. This appeared to be justified, among other things, by the fact that values of critical exponents obtained for these compounds were usually close to those resulting from the Landau theory. However, it was found that accurate experimental measurements made for ferroelectric crystals can give results deviating from mean-field theory. In the past two decades, papers have been published, particularly relating to TGS (see, e.g., Refs. 3–5), in which experimental results have been more or less conclusively linked to the theoretical results reported by Larkin and Khmelnitsky⁶ and Aharony.⁷

Independently of this, studies, were also conducted on the influence of lattice defects and impurities on the critical behavior of TGS and TGSe (e.g., Refs. 8–12). The contribution of defects, always present in real samples, even those which were not intentionally doped, have a marked influence on the experimental results obtained, particularly in the immediate vicinity of the Curie point. On approaching the phase-transition point, effects associated with the occurrence of the surface layers on the samples also become even more apparent.¹³ Because of these causes, appreciable deviations from mean-field theory are sometimes recorded in experiments, especially as regards the form of the observed temperature functions for various thermodynamic magnitudes close to T_c (e.g., susceptibility) and values of critical exponents.

In this paper we present our recordings of distinct deviation from mean-field theory and which, in our opinion, are not related to the presence of defects or surface layers and cannot be interpreted on the basis of the described approximate model derived from the Larkin-Khmelnitsky theory.

EXPERIMENTAL

Tests were conducted on samples on triglycine sulfate and triglycine selenate. The surfaces of the crystals were

covered with circular (partial covering of the surface) and rectangular (total covering of the surface) gold electrodes, with a mean surface of about 0.5 cm². For measurements on TGSe and TGS, for which results are shown on Figs. 1–3, samples with electrodes completely covering the crystal surfaces were used. The thickness of the tested samples lay in the interval from 1.1 to 2.2 mm. Immediately prior to measurements, the crystals were heated for some tens of hours at a temperature of about 85°C $\approx T_c + 35^\circ\text{C}$ (TGS crystals) and about 30°C

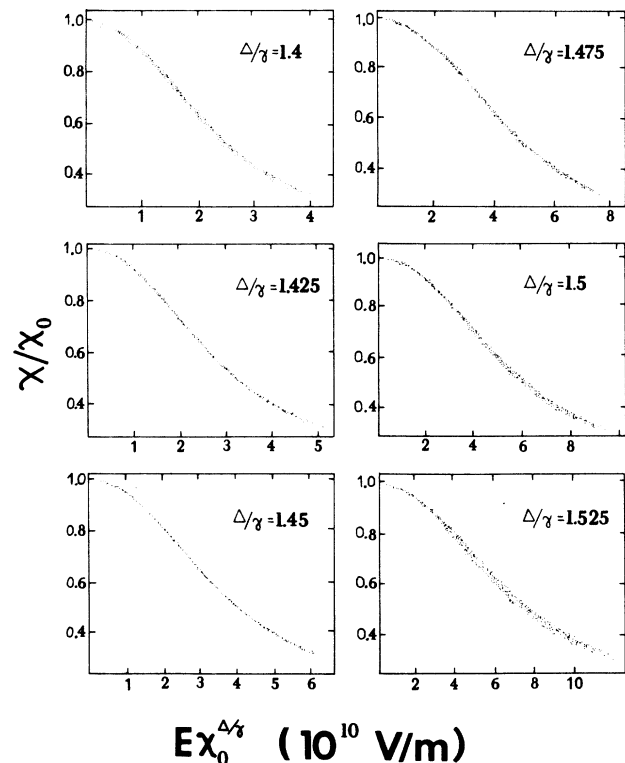


FIG. 1. Function $\chi\chi_0^{-1}$ vs $E\chi_0^{\Delta/\gamma}$ for TGSe for various values of the critical exponents ratio Δ/γ . The experimental points have been obtained from measurements of the relations χ vs E (on an average about 20 values of E for each temperature) at 16 temperatures in the interval corresponding to $10^{-3} < (T - T_c)/T_c < 10^{-2}$ and at the pressure $p = 57 \times 10^6 \text{ N m}^{-2}$.

$\approx T_c + 8^\circ\text{C}$ (TGSe crystals).

Measurements were made of the relation between paraelectric susceptibility and the constant external field E at a determined pressure and temperature of the oil surrounding the sample. The frequency of the measuring field E_m of the capacitance meter was 1 kHz, while the

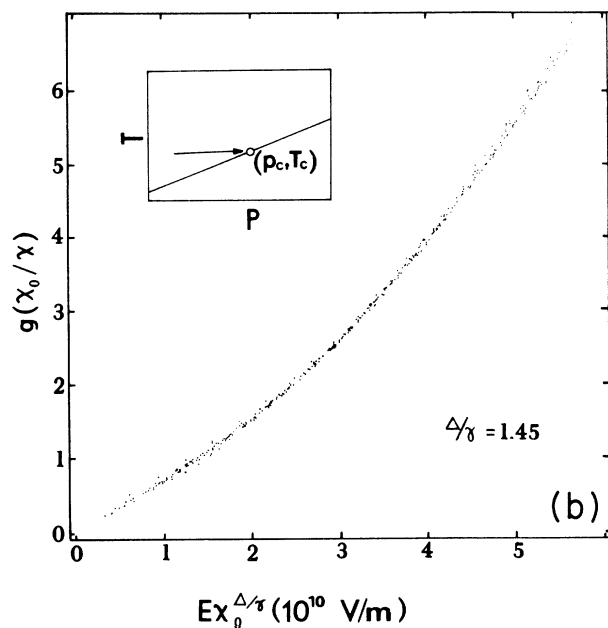
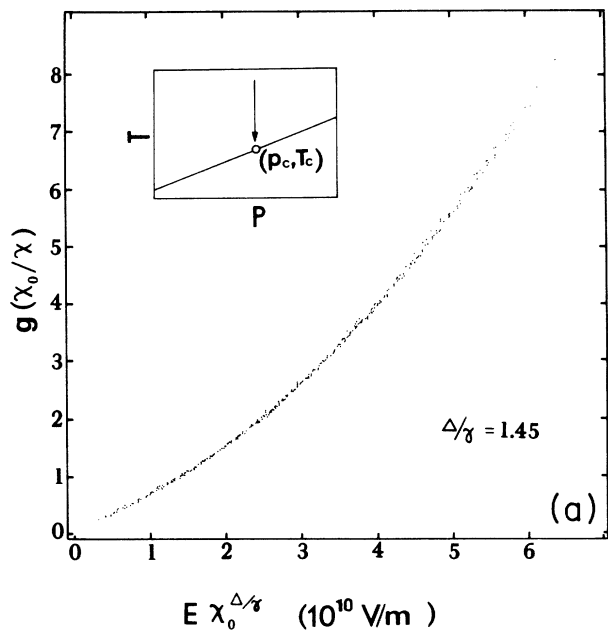


FIG. 2. Function $g(\chi_0/\chi)$ vs $E\chi_0^{1/45}$ for TGSe. Values of χ_0 and $\chi(E)$ have been determined for (a) $p = 57 \times 10^6 \text{ N m}^{-2}$, 16 temperatures in the interval corresponding to $10^{-3} < (T - T_c)/T_c < 10^{-2}$, and on an average about 20 values of E for each temperature, and (b) 17 pressures in the interval corresponding to $0.2 < (p_c - p)/p_c < 0.7$, $T = 298 \text{ K}$, and on an average about 20 values of E for each pressure. Insets: diagrammatic scheme of the line of critical points. Arrows indicate the paths by which the critical point with coordinates ($p \approx 57 \times 10^6 \text{ N m}^{-2}$, $T \approx 298 \text{ K}$) was reached.

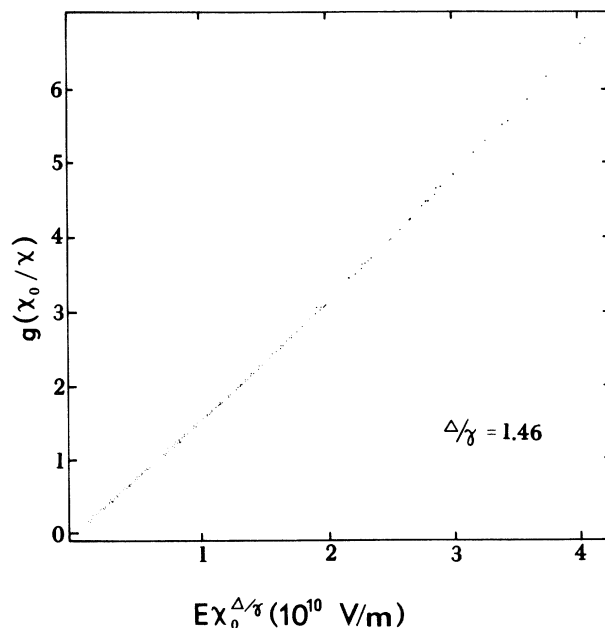


FIG. 3. Function $g(\chi_0/\chi)$ vs $E\chi_0^{1/46}$ for TGS. Values of χ_0 and $\chi(E)$ have been determined for the atmospheric pressure, 18 temperatures in the interval correspond to $10^{-3} < (T - T_c)/T_c < 10^{-2}$, and on an average about 10 values of E for each temperature.

amplitude did not exceed 1 kV/m. Both the field E with an amplitude of a few hundred kilovolts per meter and the field E_m were applied parallel to the ferroelectric axis of the crystals. Values of susceptibility χ and electric field strength E were found basing on measurements of, respectively, capacitance C and voltage U between the electrodes on the sample, making use of the formulas $\chi = \epsilon - 1 = C/C_g - 1$ (for the compounds tested here, near the Curie point $C/C_g \gg 1$, and hence $\chi \approx \epsilon$, where ϵ is the electrical permittivity), and $E = U/d$, where C_g is the geometric capacity (i.e., without the sample) of the measurement capacitor and d is the distance between the electrodes. Based on measurements of χ as a function of E for the tested compounds, the scaling functions were determined experimentally.

RESULTS AND DISCUSSION

An accurate experimental method of checking deviations from mean-field theory (MFT) is to examine the susceptibility scaling function. According to MFT, when we take into account only second- and fourth-power polarization terms in the free-energy expansion, the relation $\chi\tau^\gamma$ versus $E\tau^{-\Delta}$ is the scaling function for $\gamma = 1$ and $\Delta = 1.5$. In this case the experimental values of $\chi\tau^\gamma$ plotted as a function of $E\tau^{-\Delta}$ for various temperatures and electric fields E and also for $\gamma = 1$ and $\Delta = 1.5$ should lie on the one curve. From the point of view of the experimenter, it is more convenient, however, to study the universal scaling function χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ obtained due to substituting τ for $\chi_0^{-1/\gamma}$ in the algebraic terms $\chi\tau^\gamma$ and $E\tau^{-\Delta}$ in accordance with relation $\chi_0 \sim \tau^{-\gamma}$. The ad-

vantage of making this substitution is that the results obtained do not carry any significant error introduced in determination of the critical temperature. Naturally, this substitution is only feasible when we have to deal with a power function of χ_0 versus τ . If this condition is satisfied (as, for instance, in the case of MFT), it may be expected that the experimental function χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ for appropriate γ and Δ will also determine a scaling function, on condition that the system considered behaves so as to satisfy the static scaling hypothesis.

In the case of the TGS and TGSe ferroelectrics, we have to deal with a line of critical points $T_c(p)$, where p is the hydrostatic pressure. Hence a given point on the line $T_c(p)$ may be approached along various paths lying in the p - T plane. For TGSe we made two kinds of measurements in the paraelectric phase. On one side we tested the relation χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ in the situation where χ and χ_0 were measured at various temperatures but with constant pressure $p = 57 \times 10^6 \text{ N m}^{-2}$ [see inset of Fig. 2(a)]. For this pressure $T_c \cong 298 \text{ K}$. On the other side we made similar measurements at a constant temperature $T \cong 298 \text{ K}$ for various hydrostatic pressures [see inset of Fig. 2(b)]. In both cases, for a given constant temperature or pressure, the susceptibility χ was determined for about 20 values of the field E . In this way the scaling function was tested in the situation where the same point with coordinates $(57 \times 10^6 \text{ N m}^{-2}, 298 \text{ K})$ was approached from two mutually perpendicular paths on the p - T plane. For the pressure applied ($10^5 \text{ N m}^{-2} < p < 60 \times 10^6 \text{ N m}^{-2}$) the relation T_c versus p in TGSe is linear (see Ref. 14), i.e., $T_c = T_c(p_{\text{atm}}) + Kp$, where $K > 0$. For measurements made at various pressures, the earlier mentioned substitution of $\chi_0^{-1/\gamma}$ for τ in the argument of the scaling function corresponds to the substitution of $\chi_0^{-1/\gamma}$ for $\pi = (p_c - p)/p_c$ (cf. Ref. 15). In this way, for both temperature and pressure relations, we obtain a common magnitude $\chi_0^{-1/\gamma}$, which is a measure of the distance from the critical point.

For TGS similar measurements were made at various temperatures in the paraelectric phase but at atmospheric pressure. In the case of the tested samples, both TGS at atmospheric pressure $p = p_0$ and TGSe at $p \neq p_0$, the range of measurement temperatures corresponded to the reduced temperature $10^{-3} < \tau = [T - T_c(p)]/T_c(p) < 10^{-2}$. For TGSe, when testing the pressure relation, the range of reduced pressures had a value $0.2 < \pi < 0.7$ for $T = 298 \text{ K}$.

In Fig. 1 are shown examples of relations χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ for TGSe for various Δ/γ in the case of temperature measurements at constant pressure. As may be seen, the best concentration of points about a single curve is found for $\Delta/\gamma \cong 1.45$. Similarly, it was possible from the data obtained from pressure measurements at constant temperature to ascertain that also in this case the relation χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ has the nature of the scaling function for $\Delta/\gamma \cong 1.45$. On the basis of a similar analysis of the scaling functions obtained experimentally from a few temperature measurements at atmospheric pressure of two TGS samples with electrodes partially and completely covering the surfaces of the crystals, an estimated in-

terval $1.45 \leq \Delta/\gamma \leq 1.475$ was found.

These obtained results give evidence that values of the quotients Δ/γ for both samples diverge slightly from the value resulting from mean-field theory, i.e., $\Delta/\gamma = 1.5$. These deviations are only slight, and for this reason their interpretation requires a certain caution. In the literature it is stressed that both lattice defects and impurities may lead to deviations from mean-field theory. We performed additional measurements of the relation χ/χ_0 versus $E\chi_0^{\Delta/\gamma}$ for TGS crystals grown from aqueous solutions containing 0.1% and 1% Cr_2SO_4 , and thus for samples in a certain sense intentionally defected, i.e., doped with chromium ions. With an accuracy equal to the measurement error, values of Δ/γ the same as for pure TGS crystals were found.¹⁶ Additional temperature measurements were also made at atmospheric pressure for a few TGSe crystals of different quality and for both kinds of electrodes. The most probable value $\Delta/\gamma \cong 1.45$ obtained from these measurements is less than the classical value of 1.5.

As already mentioned, there is also another possibility of interpreting the Δ/γ values found. For this purpose we may make use of the approximate model³ derived from Larkin-Khmelnitsky theory.⁶ This model is based on the expansion of the free energy F_{LK} with an accuracy to the fourth polarization power. For $T > T_c$ we have

$$F_{\text{LK}} = \frac{1}{2}\alpha_0\tau q(\tau)P^2 + \frac{1}{4}\beta_0q^3(\tau)P^4 - \frac{1}{6}\gamma_0\tau^2[1/q(\tau) - 1], \quad (1)$$

where $\alpha_0, \beta_0, \gamma_0$ are constants and

$$q(\tau) = [1 - 3b \ln(\tau/\tau_0)]^{-1/3}, \quad (2)$$

where b, τ_0 are parameters. For $b=0$ the free energy (1) takes the classical Landau energy form. Taking into account that for small $3b \ln(\tau/\tau_0)$,

$$q(\tau) \cong (\tau/\tau_0)^b, \quad (3)$$

we may write the scaling function $\chi/\chi_0 = f(E\chi_0^{\Delta/\gamma})$ in the form

$$\chi/\chi_0 = f(E\chi_0^{1.5/(1+b)}). \quad (4)$$

Hence we obtain for the model (1) in the approximation (3) a value $\Delta/\gamma = 1.5/(1+b)$, since from the form of the energy (1) for $q = (\tau/\tau_0)^b$ it is clear that $\Delta = 1.5$ and $\gamma = 1+b$. The values of Δ/γ we obtained are in agreement with the value $b = 0.036$ quoted for TGS in Ref. 3, as after substitution we get $\Delta/\gamma = 1.5/(1+b) = 1.5/(1+0.036) \cong 1.45$.

The values we obtained for Δ/γ differ only slightly from those predicted by mean-field theory. Therefore, we would like to present more convincing arguments for the existence of deviations from this theory and also from the model based on expansion (1). From the form of the free energy (1), taking into account the approximation (3), the following relation may be found:

$$g(\chi_0/\chi) = (27\beta_0\alpha_0^{-3b/\gamma}\tau_0^{3b(b/\gamma-1)})^{1/2}E\chi_0^{\Delta/\gamma}, \quad (5)$$

where

$$g(x) = (x+2)(x-1)^{1/2}.$$

Therefore, $g(\chi_0/\chi)$ as a function of $E\chi_0^{\Delta/\gamma}$ should have a linear form. However, in Figs. 2(a) and 2(b) may be seen a clearly nonlinear form of $g(\chi_0/\chi)$ versus $E\chi_0^{\Delta/\gamma}$ for TGSe for temperature and pressure measurements, respectively [see inserts in Figs. 2(a) and 2(b)]. A clear, though considerably smaller, nonlinearity may be observed for TGS in Fig. 3.

The expression $g(\chi_0/\chi)$ depends only on the quotient χ/χ_0 . Hence we may consider it as a scaling function of the argument $E\chi_0^{\Delta/\gamma}$. Thus in Figs. 2 and 3 may be seen the scaling nature of the presented functions obtained for appropriate Δ/γ values. The nonlinearity of the presented relations cannot be explained based on the energy (1) either for $b \equiv 0$, i.e., as in mean-field theory, or for $b \neq 0$, as for the approximate model derived from Larkin-Khmelnitsky theory. From mean-field theory we have [cf. Eq. (5) for $b=0$]

$$g(\chi_0/\chi) \sim E\chi_0^{3/2}, \quad (6)$$

and for the model based on expressions (1) and (2),

$$g(\chi_0/\chi) \sim E\chi_0^{3/2} [1 - 3b \ln(\tau/\tau_0)]^{-1/2}, \quad (7)$$

while for the model based on expression (1) with approximation (3), we have

$$g(\chi_0/\chi) \sim E\chi_0^{\Delta/\gamma}, \quad (8)$$

where Δ/γ may be estimated similarly as in the case of Fig. 1.

It is obvious that neither the relations (6) and (7) nor (8) correspond to the presented curve forms, particularly those in Figs. 2(a) and 2(b) for TGSe and also in Fig. 3, although for TGS the nonlinearity is less pronounced.

CONCLUSIONS

In this paper we wished to show deviations from mean-field theory and from the approximate model based on Larkin-Khmelnitsky theory in TGS and TGSe. Our results are of particular significance in that, to the best of our knowledge, these are the two models which were most often used to describe the critical properties of the very popular TGS and TGSe ferroelectrics.

The experimental results presented in this paper show clearly that the free energy $F(\tau, P)$ of the tested com-

pounds is a nonanalytical function. This conclusion is derived from the following reasoning. The free energy for any microscope model (Ising, etc.) calculated in approximation of the molecular field or obtained in the form of a series expansion (without extrapolation using the Padé approximant) has the form of an infinite series:

$$F = \frac{1}{2}\alpha_0\tau P^2 + \frac{1}{4}\beta_0 P^4 + \sum_{n=3}^{\infty} \frac{1}{2n} C_{2n} P^{2n}, \quad (9)$$

where the coefficients $\alpha_0, \beta_0, C_{2n}$ are certain constants. If the constants $\alpha_0, \beta_0, C_{2n}$ are positive, we have a stable critical point. It may be demonstrated that terms with P^{2n} ($n \geq 3$) give singularity in the susceptibility of several orders less than terms with P^2 and P^4 . Therefore, in the vicinity of the critical point of significance are only two components of the free energy, with P^2 and P^4 (Landau theory for the second-order phase transitions). They give a susceptibility scaling function (5) for $b=0$, while higher-order terms of the free energy are a source of corrections to the scaling function, which could possibly be visible in the experiment beyond the critical region as deviations from scaling. In Fig. 1–3 these deviations cannot be ascertained despite the only slight broadening of the experimental points associated probably with measurement errors. In order to get nonlinearity in the argument of $E\chi_0^{\Delta/\gamma}$ on the right-hand side of Eq. (5) in agreement with our experimental results, the higher-order terms of the free energy, P^6, P^8, \dots , must give a contribution to the scaling (and not corrections to scaling of lesser singularities) of the same order as given by the terms P^2 and P^4 . It may be shown that the scaling contribution of the terms P^6, P^8, \dots is only possible when the coefficients C_6, C_8, \dots in (9) are not constants (as in the Landau theory), but are dependent on τ in a specific singular manner.

ACKNOWLEDGMENTS

The authors wish to express their thanks to Professor Jadwiga Stankowska of the Adam Mickiewicz University in Poznań for making available a TGSe single crystal. This work was supported by The Institute for Low Temperature and Structure Research of The Polish Academy of Science from the funds of The Central Programme for Basic Research on "Structure, Phase Transitions and Properties of Molecular Systems and Condensed Phases" (CPBP 01.12).

¹J. A. Gonzalo, Phys. Rev. B **1**, 3125 (1970).

²M. J. Tello, E. H. Bocanegra, J. Peraza, and J. Manas-Diaz, J. Phys. Soc. Jpn. **41**, 1681 (1976).

³Th. Natterman, Phys. Status Solidi B **85**, 291 (1978).

⁴K. H. Ehses and H. E. Müser, Ferroelectrics **12**, 247 (1976).

⁵K. Deguchi, J. Phys. Soc. Jpn. **47**, 153 (1979).

⁶A. I. Larkin and D. E. Khmelnitsky, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys. JETP **29**, 1223 (1969)].

⁷A. Aharony, Phys. Rev. B **8**, 3363 (1973).

⁸A. P. Levanyuk, V. V. Osipov, A. S. Sigov, and A. A. Sobyannin, Zh. Eksp. Teor. Fiz. **76**, 345 (1979) [Sov. Phys. JETP **49**, 179 (1979)].

⁹J. Stankowska, Acta Phys. Pol. A **64**, 115 (1983).

¹⁰A. Pawlowski and B. Hilczer, Acta Phys. Pol. A **67**, 673 (1985).

¹¹B. A. Strukov, S. A. Taraskin, K. A. Minaeva, and V. A. Fedorikhin, Ferroelectrics **25**, 399 (1980).

¹²K. H. Ehses and H. Wern, Ferroelectrics **54**, 277 (1984).

¹³T. Sekido and T. Mitsui, J. Phys. Chem. Solids **28**, 967 (1967).

¹⁴F. Jona and G. Shirane, Phys. Rev. **117**, 139 (1960).

¹⁵B. Fugiel, K. Ćwikiel, and J. Zioło, Phys. Rev. B **36**, 3963 (1987).

¹⁶B. Fugiel, B. Westwański, and J. Zioło (unpublished).