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The equation-of-state parameters of triglycine sulphate (TGS) ferroelectric for both phases near the critical point

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Abstract. The experimental electric susceptibility isotherms (that is, the electric susceptibility versus electric field dependences) were obtained for temperatures over the interval $-4 \text{ K} < T - T_c < 7 \text{ K}$. The constant coefficients A , B and C of the equation of state $E = A\tau P + BP^3 + CP^5$ were found separately for the paraelectric and ferroelectric phases on the basis of precise susceptibility measurements. The validity of the singular part of the Landau equation of state $E = A\tau P + BP^3$ was checked. The parameter s , where $s = 1$ for $\tau > 0$ and $s \approx 4/3$ for $\tau < 0$, which determines the modified equation of state $E/s = A\tau P + BP^3$ for temperatures not too close to T_c , has been introduced.

1. Introduction

Triglycine sulphate (TGS) crystals are among the rare examples of ferroelectric materials which undergo continuous phase transitions. For this reason, investigations of their critical behaviour are very important. The dielectric properties of TGS near the Curie point are almost always described on the basis of Landau theory (references [1–3]). The tunnelling effect has also been taken into account in references [4, 5], as have logarithmic corrections in references [6–12]. Up to now, however—for both the paraelectric and the ferroelectric phases—the majority (according to our estimation, about 90%) of the experimental results for this crystal have been compared with the singular part of the Landau equation of state:

$$E = A\tau P + BP^3 \quad (1)$$

where E is the electric field, P is the polarization, and $\tau = (T - T_c)/T_c$ is the reduced temperature, while A and B are constant coefficients. Such a P^3 -model (maximally the third power of P appears in the equation of state) is usually assumed to be valid over an interval of a few degrees around the critical temperature T_c . Formula (1) is in accordance with the static scaling hypothesis. This means that pure power functions for critical dependences can be obtained from it (hence the denomination ‘singular’). The mean-field-approximation values of the critical exponents, e.g. $\beta = 1/2$, $\delta = 3$, and $\gamma = \gamma' = 1$, are valid in this case. Many previous classical polarization measurement results for TGS substituted into the relations $P \sim (-\tau)^\beta$ and $E \sim P^\delta$ confirm such values of β and δ , although with rather low accuracy. The higher-order terms involving P^5 , P^7 , P^9 , ... added to (1) give corrections to the scaling.

Up to now, the same values of the equation-of-state parameters A and B have been used for both phases. Moreover, parameters obtained experimentally for the paraelectric and ferroelectric phases were sometimes inserted into the same equation of state. In this paper

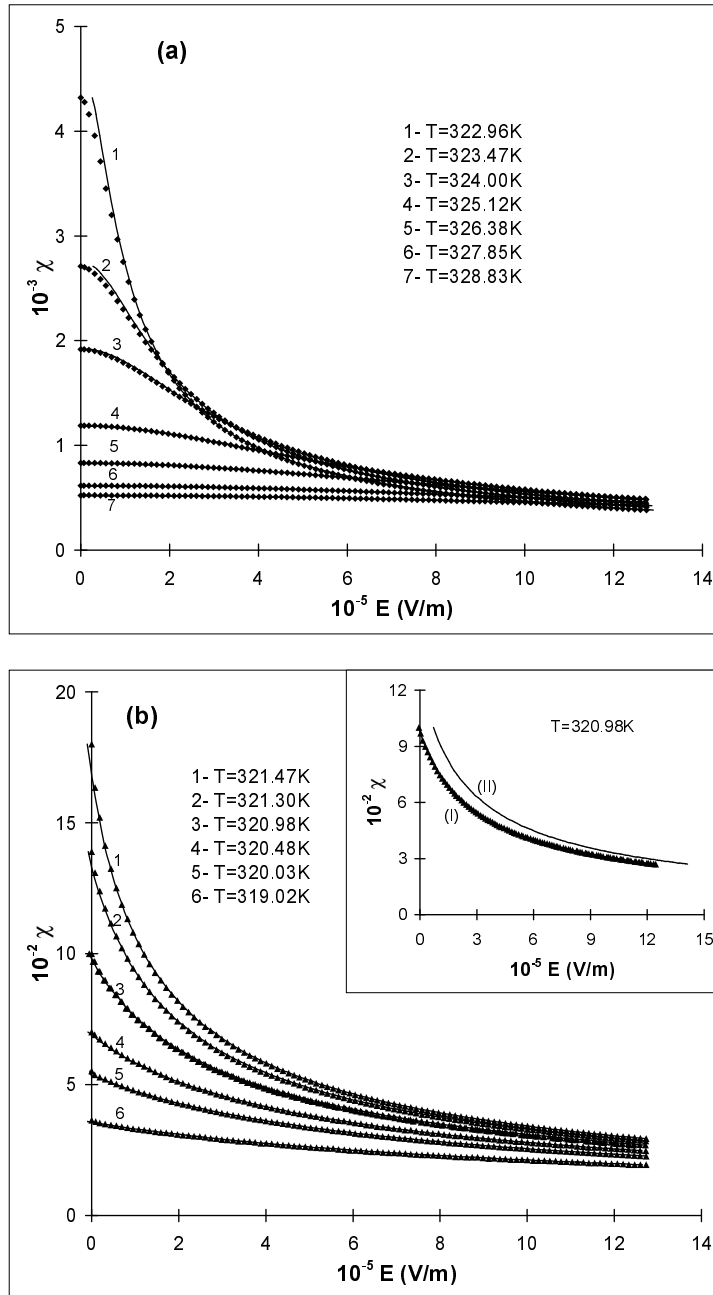


Figure 1. Experimental electric susceptibility isotherms for the paraelectric (diamonds; seven temperatures are given in (a)) and ferroelectric (triangles; six temperatures are given in (b)) phases; the solid lines correspond to: (a) the P^5 -model fit for $T > T_c$; (b) the P^5 -model fit for $T < T_c$; (c) the P^3 -model fit for $T > T_c$; (d) the P^3 -model fit for $T < T_c$; inset in (b): experimental results for $T = 320.98 \text{ K} < T_c$ and two curves obtained numerically for the P^5 -model: (I) for $T_c = 322.22 \text{ K}$ and $A = A_f$, $B = B_f$, $C = C_f$ given in section 3.2 (the experimental and fitted dependences coincide); and (II) for $T_c = 322.23 \text{ K}$ and $A = A_p$, $B = B_p$, $C = C_p$ given in section 3.2.

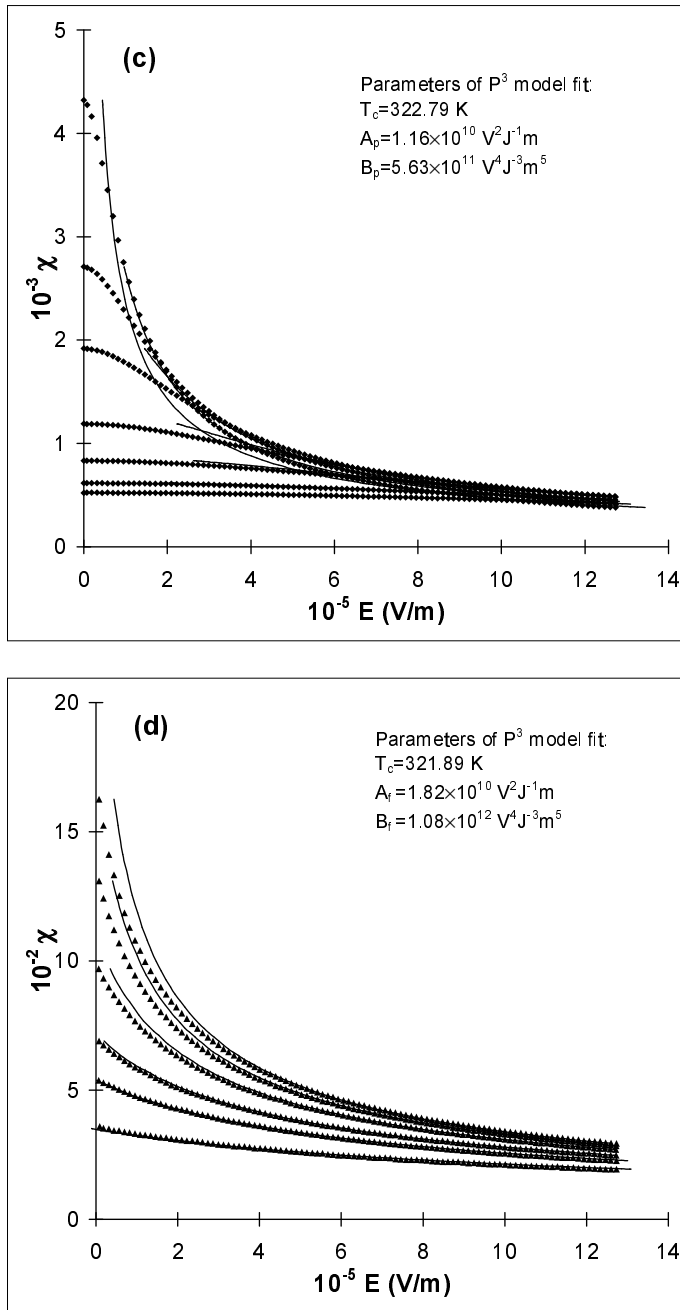


Figure 1. (Continued)

we show that such a procedure may lead to incorrect conclusions. Below, we present an experimental method for carrying out non-linear susceptibility investigations which allows us to compare the results obtained for paraelectric and ferroelectric phases *quantitatively*.

The electrical susceptibility χ is a physical variable which can be measured very

accurately. Experimental investigations of the initial (for $E = 0$) electric susceptibility χ_0 of the paraelectric phase are sufficiently precise to confirm the Curie–Weiss law $\chi_0 = \text{constant}/(T - T_c)$ (i.e. $\gamma = 1$) with satisfactory accuracy. However, such results, for χ_0 above T_c , do not give any information about the full equation of state. Only the coefficient A in (1) can be determined in this case. On the other hand, analogous zero-field susceptibility investigations of the ferroelectric region may provide—due to the non-zero spontaneous polarization—data concerning not only A but also coefficients of higher order, even ones not appearing in (1). However, the results obtained for temperatures below T_c are not consistent with those measured for the paraelectric phase. For example, the experimental values of the amplitude ratio Γ/Γ' presented in various papers are larger than 2, whereas $\Gamma/\Gamma' = 2$ is the result from (1), and Γ, Γ' are taken from the formulae

$$\chi_0 = \Gamma\tau^{-1} \quad \text{for } T > T_c \quad (2a)$$

$$\chi_0 = \Gamma'(-\tau)^{-1} \quad \text{for } T < T_c. \quad (2b)$$

In reference [13] the results of Γ/Γ' measurements for three TGS samples are 3.0, 2.3, and 2.7. Such differences and deviations from $\Gamma/\Gamma' = 2$ have been explained as being caused by the motion and clamping of ferroelectric domains as well as by the rather adiabatic conditions prevailing during a.c. susceptibility measurements (causing the difference between the isothermal and adiabatic susceptibilities below T_c). According to reference [13], the expected experimental value of Γ/Γ' , including the adiabatic correction, should be equal to 2.4. Such a result ($\Gamma/\Gamma' = 2.42$) has been obtained by Gonzalo (reference [14]). In our opinion, in addition to the factors mentioned above, the terms involving higher-than-third powers of the polarization P in the equation of state can also modify the experimental value of Γ/Γ' . However, such a correction cannot be large in the case of TGS for temperatures a few degrees below T_c . As will be shown below, the measurement conditions, i.e. the rate of temperature change during cooling or heating as well as the history of the sample left in the ferroelectric phase (the aging processes), may have an influence on the experimental values of Γ/Γ' (see figure 3, later).

The experimental determinations of the Γ/Γ' amplitude ratio are examples of investigations which allow us to compare the corresponding parameters of the equation of state for the two phases. As has been mentioned above, the same values of A, B, \dots have been assumed for the two phases up to now. The coefficient A in equation (1) has usually been obtained from the Curie–Weiss law, i.e. from measurements for temperatures above T_c , while B has been taken from the temperature dependence of the spontaneous polarization (equation (6)).

2. Experiment

In the present paper we investigate the equation of state for TGS separately for the two phases (near T_c), availing ourselves of the results obtained using the same experimental method for both phases. The electric field dependences of the electric susceptibility have been measured. The constant electric field parallel to the ferroelectric axis was lowered in steps from 1266 kV m^{-1} to 0. The step size was about 12.7 kV m^{-1} . The amplitude and frequency of the measuring field of the TESLA BM 595 LCR meter were 0.063 kV m^{-1} and 1 kHz, respectively. A similar measurement circuit was shown in reference [15]. We have chosen one of the highest quality samples from among crystals that we had. It was grown from a water solution at $52 \text{ }^\circ\text{C}$, i.e. in the paraelectric phase, by the standard method (see, e.g., [16]). Using an x-ray method, and optical and electron microscope analysis, we found no deviations from the crystallographic structure and no major defects in our crystals.

A relatively very high maximum susceptibility at the critical temperature T_c as well as—within the limits of the experimental error $\Delta T \approx 10^{-2}$ K—no temperature hysteresis have been observed. The rectangular surface of the sample was 35.5 mm^2 and its thickness was 0.79 mm . The isotherms measured by us at various temperatures are shown in figure 1.

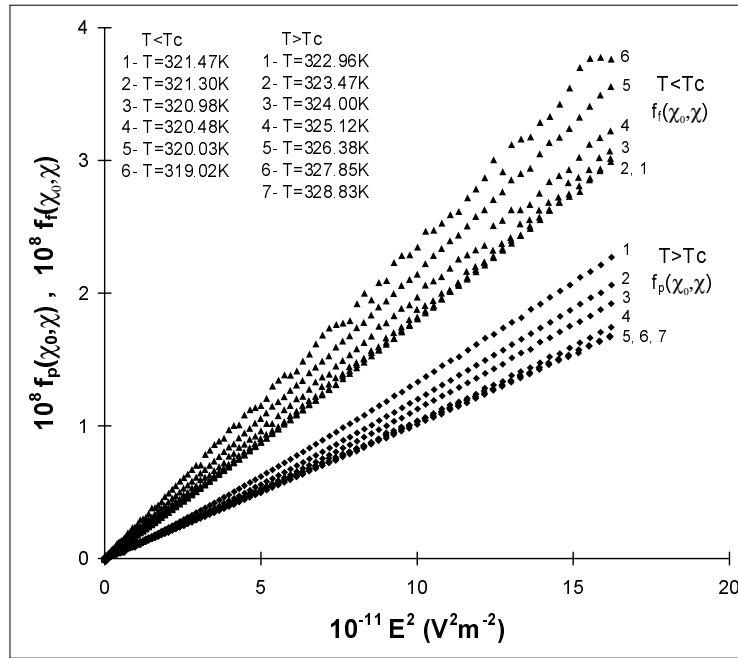


Figure 2. The functions $f_f(\chi, \chi_0) = 1/\chi^3 - 3/(2\chi^2\chi_0) + 1/(2\chi_0^3)$ for $T < T_c$ (triangles) and $f_p(\chi, \chi_0) = 1/\chi^3 + 3/(\chi^2\chi_0) - 4/\chi_0^3$ for $T > T_c$ (diamonds) versus E^2 .

3. Results

3.1. Deviations from scaling Landau behaviour

In figure 2, the validity of equation (1) is checked for both phases. As the electric susceptibility isotherms were measured, the recasting of formula (1) into a relation between E and χ (not P) was required. The following relations (reference [17, 18]) have been used:

$$\frac{1}{\chi^3} + \frac{3}{\chi^2\chi_0} - \frac{4}{\chi_0^3} = 27\varepsilon_0^3 B E^2 \quad (3a)$$

for the paraelectric phase and

$$\frac{1}{\chi^3} - \frac{3}{2\chi^2\chi_0} + \frac{1}{2\chi_0^3} = 27\varepsilon_0^3 B E^2 \quad (3b)$$

for the ferroelectric region. After inserting the experimental data, i.e. the points from various isotherms, into (3a) and (3b), we were able to check the validity of equation (1). According to (3a) and (3b), the experimental dependences

$$f_p(\chi, \chi_0) = \frac{1}{\chi^3} + \frac{3}{\chi^2\chi_0} - \frac{4}{\chi_0^3}$$

versus E^2 and

$$f_f(\chi, \chi_0) = \frac{1}{\chi^3} - \frac{3}{2\chi^2\chi_0} + \frac{1}{2\chi_0^3}$$

versus E^2 should form one—the same for both phases—linear dependence. However, we can see in figure 2 that splitting and slight non-linearities (visible only if we inspect the curves in the diagrams very carefully) arise as a result of the influence of higher-order terms in the equation of state. Such an effect has been discussed in our previous papers (cf. reference [19]) but only for the paraelectric region. The interpretation extended beyond the mean-field approximation has been examined (e.g. references [19–21]). However, assuming that Landau behaviour obeying the singular part of equation of state (1) occurs in the limit $E \rightarrow 0$ in figure 2, we can see that the B -parameter obtained for very small E seems to be different for the two phases—similarly to the case for the parameter A .

3.2. Parameters of the equation of state

Below, we compare the equations of state for the two phases: paraelectric and ferroelectric. We check the validity of the classical P^5 -model (maximally the fifth power of P appears in the equation of state) with constant A , B , and C :

$$E = A\tau P + BP^3 + CP^5 \quad (4)$$

$$\frac{\partial E}{\partial P} = 1/(\varepsilon_0\chi) = A\tau + 3BP^2 + 5CP^4. \quad (5)$$

The term containing P^5 in equation (4) has been added due to the deviations from the Landau P^3 -model (equation (1)) in figure 2. On the basis of (4) and (5), we can calculate the function of two variables $E = E(\chi, T)$ with the parameters A , B , C , and T_c (equation (A2) in the appendix). By fitting the relation $E = E(\chi, T)$ to the experimental data, separately above and below T_c , we obtained the values

$$A = A_p = (1.062 \pm 0.003) \times 10^{10} \text{ V}^2 \text{ J}^{-1} \text{ m}$$

$$B = B_p = (5.02 \pm 0.02) \times 10^{11} \text{ V}^4 \text{ J}^{-3} \text{ m}^5$$

$$C = C_p = (5.2 \pm 0.2) \times 10^{14} \text{ V}^6 \text{ J}^{-5} \text{ m}^9$$

$$T_c = 322.23 \pm 0.02 \text{ K}$$

for the paraelectric phase and

$$A = A_f = (1.423 \pm 0.006) \times 10^{10} \text{ V}^2 \text{ J}^{-1} \text{ m}$$

$$B = B_f = (6.59 \pm 0.07) \times 10^{11} \text{ V}^4 \text{ J}^{-3} \text{ m}^5$$

$$C = C_f = (4.71 \pm 0.06) \times 10^{14} \text{ V}^6 \text{ J}^{-5} \text{ m}^9$$

$$T_c = 322.22 \pm 0.01 \text{ K}$$

for the ferroelectric phase. The fitting procedure has been carried out simultaneously for all temperatures and electric fields for each phase, and the errors are standard deviations. The real precision is lower, i.e. of the same order as those achieved by other authors (cf. table 1). The fitting curves have been shown as solid lines in figure 1. The experimental points for $E = 0$ for the ferroelectric phase have been excluded from the fitting procedure because, for $E = 0$ and $\tau < 0$, two equivalent thermodynamic states ($P^+ > 0$ and $P^- < 0$, $|P^+| = |P^-|$) exist, and thus the experimental values of P and χ may be not unequivocal. In the inset of figure 1(b), the experimental isotherm for $T = 320.98 \text{ K} < T_c$ as well as two theoretical curves (for the Landau P^5 -model) for the same temperature but for two

sets of A -, B -, C -parameters, i.e. obtained for the paraelectric and ferroelectric phases, are presented.

For comparison, the validity of a Landau P^3 -model (equation (1)) has been checked for the same temperatures, and this is shown in figures 1(c) and 1(d). Two sets of T_c -, A -, and B -parameters have been fitted for the two phases and are shown in the figures. The relation $E = E(\chi, T)$, equation (A3), obtained from (1) and included in the appendix, is now used (notice that, for clarity, fitted solid lines have been drawn for the same intervals of χ as in the experiment). One can see that marked deviations from model (1) have been obtained. Moreover, the difference of about 0.9 K between the T_c -values that has arisen from the fitting for the paraelectric and ferroelectric phases is too large compared with that (of 10^{-2} K) for T_c presented in section 3.2 for equation (4). Also, for fixed $T_c = 322.225$ K, the two-parameter (A , B) fits are much worse than those in figures 1(a) and 1(b). Such results enable us to state that over the whole temperature region investigated (of about 11 K), higher-order terms should also be taken into account (cf. the inset of figure 3(b)). This means that the singular part (1) of the equation of state can be obtained at best by an extraction of the P - and P^3 -terms from the previously fitted more complex formula (4). Any direct fitting of purely P^3 -model parameters closer to T_c and for very small E cannot give correct results due to ‘rounding effects’, i.e. drastic deviations from theoretically predicted temperature dependences of the susceptibility caused by defects (reference [22, 23]), surface layers (reference [24]) and so on.

4. Discussion

The differences between the corresponding parameters A , B , and C obtained for the two phases are rather unexpected, because up to now the same equation of state has been assumed to apply on both sides of T_c (the experimental fact that $\Gamma/\Gamma' \neq 2$ has been underrated!) The coefficients C measured by us are rather effective parameters, because their values may be influenced by terms of higher order than P^5 . It is interesting that, for the coefficient values given above, the ratios $A_f/A_p = 1.34 \pm 0.01$ and $B_f/B_p = 1.31 \pm 0.02$ are similar to each other and approximately equal to $4/3$. It should be stressed that the factor $4/3$ has also been obtained recently by us for the tricritical point of triglycine selenate (TGSe) ferroelectric (reference [25]).

The question arises of whether the factor $4/3$ can be treated as a universal quantity. Further investigation of this seems likely to be very interesting. On the other hand, we do not know how the parameters A and B change in value when passing the critical point. In figure 3(a), the experimental temperature dependences of the reciprocal susceptibilities for $E = 0$ as well as for $E = 185 \text{ kV m}^{-1}$ and $E = 375 \text{ kV m}^{-1}$ are presented. In figure 3(b), experimental and theoretical curves obtained for the model (4) with two sets of parameters given in section 3.2 and corresponding to the two phases have been shown. Also, an enlarged view of the region close to T_c has been added in the inset. The contribution of the singular part (P -, P^3 -terms) has been also presented by drawing dotted lines which correspond to model (4) with A_p , A_f , B_p , B_f , and T_c given in section 3.2, but for $C_p = C_f = 0$. It is evident that for the paraelectric phase, for E -values of the order of 10^2 kV m^{-1} , the Landau P^5 -model is not valid close to T_c (cf. the E - and T -values of isotherms 1 and 2 fitted in figure 1(a)). This is clearly visible in figure 3(b)—in particular between T_c and the field-dependent temperature $T_m(E)$ of the reciprocal-susceptibility minimum for $E > 0$ [26]. Higher-order terms or the temperature dependence of the coefficients of the equation of state—or both—should be taken into account for small $\tau > 0$ as in the case of Larkin–Khmelnitskii theory with logarithmic correction (references [6–10]) and the

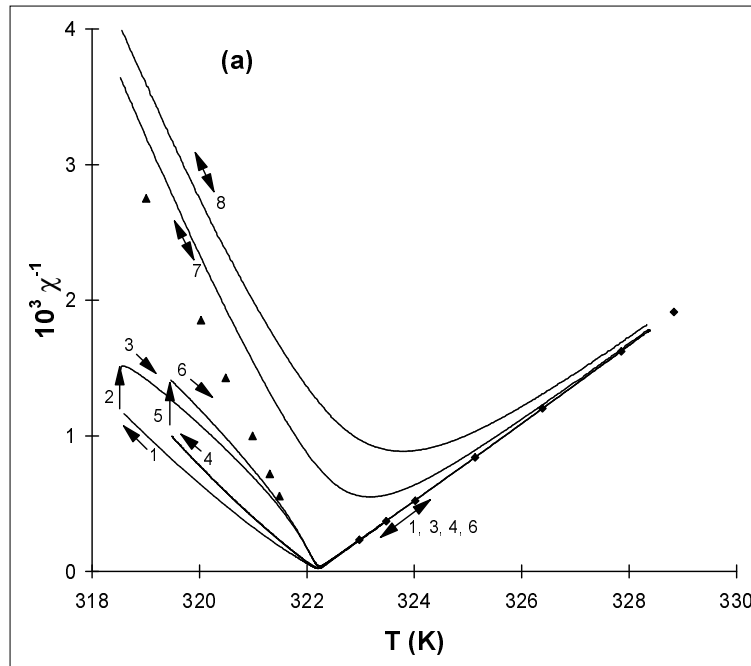


Figure 3. Reciprocal-susceptibility versus temperature dependences for $E = 0, 185$ and 375 kV m^{-1} : (a) experimental and numerical data: solid lines correspond to: cooling at the rate 0.005 K min^{-1} for $E = 0$ (1), heating at the rate 0.005 K min^{-1} for $E = 0$ (3), cooling at the rate 0.004 K min^{-1} for $E = 0$ (4), heating at the rate 0.004 K min^{-1} for $E = 0$ (6) (above T_c , all dependences obtained for $E = 0$ coincide), cooling and heating both at the rate 0.005 K min^{-1} for $E = 185 \text{ kV m}^{-1}$ (7), and cooling and heating both at the rate 0.005 K min^{-1} for $E = 375 \text{ kV m}^{-1}$ (8); arrows 2 and 5 indicate zero-field susceptibility changes at constant temperature over a period of about 24 h after coolings 1 and 4, respectively; diamonds represent experimental values of the susceptibility for $E = 0$ and $T > T_c$; triangles correspond to susceptibility values obtained numerically from equation (4) for $E = 0, T < T_c = 322.225 \text{ K}$, and A_f, B_f, C_f given in section 3.2; (b) comparison of the experimental data with the P^5 -model: solid lines—measurement results for the cooling and heating rate 0.005 K min^{-1} for $E = 0, 185, 375 \text{ kV m}^{-1}$; dashed lines—corresponding dependences obtained from equation (4) for $T_c = 322.225 \text{ K}$, A_p, B_p, C_p for $T > T_c$, A_f, B_f, C_f for $T < T_c$ given in section 3.2; dotted lines—dependences obtained from those marked by dashed lines by the removal of the terms with the coefficients C_p and C_f ; inset: an enlarged view of the region with T close to T_c and $E > 0$.

phenomenological approach with a small-power-type correction (references [19–21]). Also, other theoretical models, valid not only in the immediate neighbourhood of T_c , may be considered in this case (references [27, 28]). On the other hand, deviations from model (4) observed for experimental points obtained for small values of the parameters E and $\tau > 0$ in figure 1(a) may also be due to the fact that the measurement results obtained very close to the critical temperature differ significantly from the theoretical ones, for which the singularity $\chi_0 \rightarrow \infty$ for $\tau \rightarrow 0$ is predicted. Such experimental deviation from theory is larger above T_c , since the values of the zero-field susceptibility χ_0 for the paraelectric phase are higher than those for the same $|\tau|$ below T_c . The P^5 -model is more appropriate for the ferroelectric phase (figures 1(b), 3(b)) than for the paraelectric one. The theoretical dependences obtained on the basis of equation (4) (dashed lines) coincide with those measured below T_c for $E = 0$,

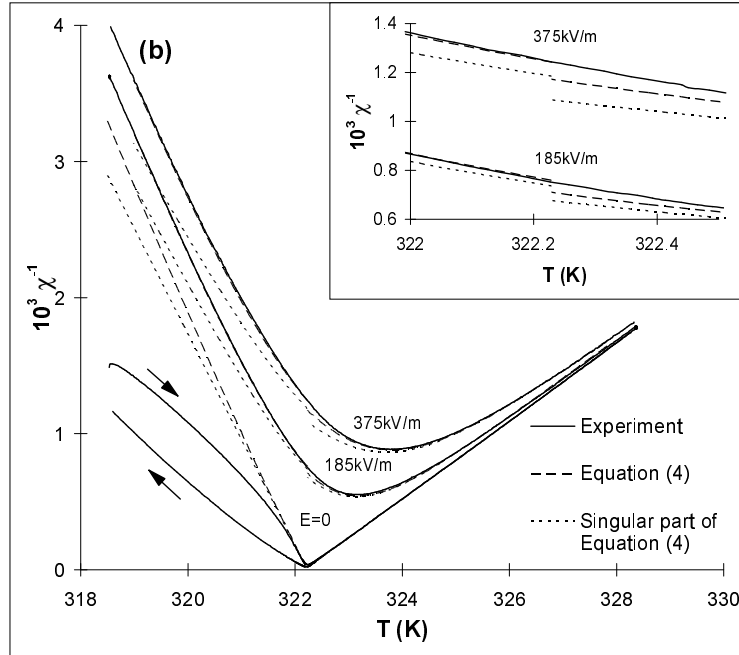


Figure 3. (Continued)

185, 375 kV m⁻¹ (figure 3(b)). The conclusion is that different behaviours are observed for the two phases for similar values of $|\tau|$ and E .

From the data presented above, we can conclude that the singular part of the Landau equation of state should be somewhat modified to the form

$$E/s = A\tau P + BP^3 \tag{1a}$$

where A, B are here the same for both phases, but $s = 1$ for the paraelectric region and $s \approx 4/3$ for the ferroelectric one. One can see that the differences between the equation-of-state parameters for the paraelectric and ferroelectric phases can also be interpreted as the modification $E \rightarrow E/s$ below T_c , e.g. as due to domain structure. A similar correction has been introduced by Gonzalo and Lopez-Alonso (reference [29]) while describing the dynamic hysteresis loop in non-equilibrium conditions. However, in our experiment the electric field was applied in steps, with a step size of 12.7 kV m⁻¹. The time for which E was kept constant (the width of one step) was 420 seconds.

The conclusion that $s > 1$ for the ferroelectric phase can be treated as a generalization of the commonly obtained non-Landau result for Γ/Γ' . According to (1a), for $s = 4/3$ we obtain $\Gamma/\Gamma' = 2s \approx 8/3 \approx 2.7$, i.e. the value often measured experimentally. Since, due to the non-zero C -coefficient, the relation of $1/\chi_0$ and T is not linear below T_c , the higher effective experimental Γ/Γ' values may be detected independently of the width of the measurement temperature interval. For example, in the case of our experimental data shown in figure 3, such a ratio might be wrongly estimated as $\Gamma/\Gamma' \approx 3$ when fitting a linear function to the χ_0^{-1} versus T dependence for the temperature range $T_c - T \approx 4$ K below T_c , i.e. where non-linearity is not clearly visible. The experimental fact that $s \approx 4/3$ in (1a) below T_c should be taken into account when comparing various parameters of equations of state obtained for different phases, not just for TGS. Up to now, as was mentioned above, in

many papers the constant A was obtained from Curie–Weiss-law measurements above T_c , while the B - and C -coefficients were obtained on the basis of fitting the following formula for the spontaneous polarization P_s :

$$P_s^2 = [-B + (B^2 - 4A\tau C)^{1/2}] / (2C) \quad (6)$$

below T_c (cf. references [13, 14]). On the other hand, the coefficient B was also determined experimentally for the paraelectric phase on the basis of the relation (cf. [13, 30])

$$\frac{1}{\chi} - \frac{1}{\chi_0} = 3\varepsilon_0 B P^2. \quad (7)$$

In table 1, the results from [13] and [14] as well as our data are compared.

Table 1. The parameters A (in $10^{-10} \text{ V}^2 \text{ J}^{-1} \text{ m}$), B (in $10^{-11} \text{ V}^4 \text{ J}^{-3} \text{ m}^5$) and C (in $10^{-14} \text{ V}^6 \text{ J}^{-5} \text{ m}^9$).

	A_p	A_f	B_p	B_f	C_p	C_f
Triebwasser [13]	1.14	—	7.4	6.5	—	3.7
Gonzalo [14]	1.02	—	—	5.6 ± 0.6	—	5.9 ± 1.5
Our data	1.06 ± 0.01	1.42 ± 0.01	5.0 ± 0.1	6.6 ± 0.1	5.2 ± 0.5	4.7 ± 0.5

The formulae (6) and (7) were usually taken into account when determining the experimental parameters A , B , C . Triebwasser (reference [13]) obtained the coefficient B both on the basis of (6) and also using relations (7) (see table 1), i.e. for the ferroelectric and paraelectric phases. The difference between the two values ($B_p > B_f$, i.e. contrary to our result) was interpreted as being a result of the adiabatic conditions prevailing in the experiment above T_c . After making an adiabatic correction (above T_c) leading to $B_p = 6.2 \times 10^{11} \text{ V}^4 \text{ J}^{-3} \text{ m}^5$, the two B -values become nearly equal.

We have presented a method for the determination of A , B , C in which the same susceptibility measurements were carried out for the two phases. Therefore the comparison of the experimental data for either side of T_c was more appropriate. The three-dimensional (χ versus E and T) fitting procedure for the A -, B -, C -, and T_c -parameters involved simultaneously all isotherms for a given phase (paraelectric or ferroelectric), i.e. 700 and 600 experimental points above and below T_c , respectively. It should be stressed that very similar values, 322.23 K and 322.22 K, for the fits at temperatures $T > T_c$ and $T < T_c$ (respectively) have been obtained numerically for T_c for TGS (we have used in further investigations $T_c = 322.225 \text{ K}$, the mean value). Since the χ versus E measurements were carried out with a very low rate of stepwise decrease of the field at constant temperature, the stationary states were investigated. If this were not the case, and the measurements had been made with temperature or field changes that were too fast, non-equilibrium values might have been observed for the ferroelectric phase (cf. figure 3(a)). Finally, we were able to control the number of relevant terms in the equation of state in a simple way, i.e. by comparison of the experimental temperature dependences of the susceptibility for various electric fields E with corresponding theoretical curves for numerically obtained values of A , B , C , and T_c (figure 3(b)).

5. Conclusions

Summing up the results for TGS obtained in this paper, we can make the following statements.

(i) Inequalities for the experimental values, $A_p < A_f$, $B_p < B_f$, where $A_f/A_p \approx B_f/B_p \approx 4/3$, have been obtained by the same a.c. susceptibility measurement method for the two phases.

(ii) For the ferroelectric phase, the equation of state $E = A_f \tau P + B_f P^3 + C_f P^5$ (in which A_f , B_f and C_f are constant) can be treated as a good approximation to the experimental data (the measurements were carried out for $0 < E < 1.3 \times 10^6$ V m⁻¹ and $T_c - T < 4$ K; see figures 1(b) and 3(b)).

(iii) For the paraelectric phase, deviations from both P^3 - and also P^5 -models with constant A_p , B_p , C_p have been confirmed for the field-dependent temperature region $T_c \lesssim T \lesssim T_m(E)$, where $T_m(E)$ is the temperature of the reciprocal-susceptibility minimum (see figure 3(b)).

(iv) The method of analysis of the experimental susceptibility data presented in this paper can be used to analyse other compounds, and not just ferroelectrics.

The important conclusion of our paper is the statement that a single set of Landau equation-of-state parameters is not suitable for describing the dielectric behaviour of TGS near the critical point. The formula (1a) has been proposed as a singular part of the equation of state. It is obvious, however, that such a Landau-type model is not valid for all τ and E . In the immediate neighbourhood of the transition point ($T = T_c$, $E = 0$), critical fluctuations play a dominant role, and deviations from equation (1a) are expected (one critical isotherm should be obtained). Unfortunately, due to the fact that we can observe in experiment barely a maximum of the zero-field susceptibility (certainly not infinity, as predicted by theory), one cannot place much reliance on the results obtained very close to T_c and for $E \approx 0$. On the other hand, the data for $E \neq 0$ in figure 3 suggest that higher-order terms in the equation of state should be added in order to explain the continuity of the reciprocal susceptibility at T_c . The conclusion is that the behaviour described by the P^3 -model does not seem to be easy to observe in experiment.

As mentioned at the beginning of this paper, the majority of experimental results have been interpreted in the framework of the simple Landau model described by equation (1) with a single set of parameters A and B . In such cases, it is particularly important for our result that $s \neq 1$ below T_c to be taken into account.

Acknowledgment

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Appendix

Solving the system of equations (4) and (5), we obtain the polarization P as a function of χ for the absolutely stable state and positive P :

$$P = \left[\frac{-3T_c B \varepsilon_0 \chi + [T_c (9T_c B^2 (\varepsilon_0 \chi)^2 + 20(T_c - T)AC (\varepsilon_0 \chi)^2 + 20T_c C \varepsilon_0 \chi)]^{1/2}}{10T_c C \varepsilon_0 \chi} \right]^{1/2}. \quad (\text{A1})$$

After substituting (A1) into (4) and factoring the equation, we get

$$E = E(\chi, T) = \sqrt{\frac{A^3}{B W^3}} (\tau W Y + 10Y^3 + Y^5) \quad (\text{A2})$$

where

$$\begin{aligned}
 W &= AC/B^2 \\
 \tau &= (T - T_c)/T_c \\
 Y &= [(9 + 20W\tau(1/(A\tau\varepsilon_0\chi) - 1))^{1/2} - 3]/10]^{1/2}.
 \end{aligned}$$

The analogous equation for the P^3 -model (equation (1)) is of the form

$$E = E(\chi, T) = \sqrt{\frac{1 - A\tau\varepsilon_0\chi}{27B(\varepsilon_0\chi)^3}}(1 + 2A\tau\varepsilon_0\chi) \quad (\text{A3})$$

for positive P .

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