Scaling and metastable behavior in uniaxial ferroelectrics

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Improved experimental resolution and computer aided data analysis of hysteresis loops at $T \approx T_C$ in uniaxial ferroelectrics triglycene sulfate (ordinary critical point), and triglycine selenate (quasitricritical point) show that scaling holds in a wide range of scaled fields spanning many orders of magnitude, well beyond the asymptotic region ($|T-T_C| \to 0$), and that the behavior of metastable *experimental* points ($E<0, P>0$) approaches the theoretical branch of the respective scaling equation as $T \to T_C$. [S0163-1829(98)05102-9]

I. INTRODUCTION

As it is well known, the revival of experimental and theoretical interest[1] in cooperative phenomena and continuous phase transitions, especially in liquid-vapor, order-disorder alloys, and magnetic systems, has stimulated a vast amount of work during the last three decades. This work includes more accurate sets of measurements close to the transitions than in previous papers, as well as the development of new theoretical concepts, such as scaling, multicritical points, and the renormalization-group theory. Ferroelectric phase transitions,[2] and, in particular, transitions in uniaxial order-disorder ferroelectrics like triglycine sulfate (TGS), have been shown[3] many years ago to present classical exponents ($\beta=\frac{1}{2}$, $\delta=3$, $\gamma=1$, $\alpha=0$) and to obey a classical (mean-field) equation of state. A prominent characteristic of this kind of transition is the role long-range dipolar interactions play in them.

More recently,[4] another uniaxial ferroelectric of the TGS family, triglycine selenate (TGSe), was found to exhibit classical tricritical exponents ($\beta=\frac{1}{4}$, $\delta=5$, $\gamma=1$, $\alpha=\frac{1}{2}$) and to follow a quasitricritical equation of state in which the tricritical exponents were used instead of the former classical critical exponents.

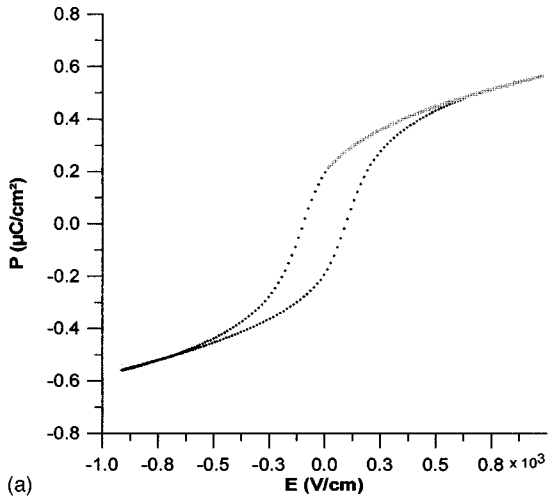
In this work we undertake, under substantially improved[3,4] experimental conditions (automated data acquisition and analysis), digital resolution in P, E, and T, a study of the equation of state of both uniaxial ferroelectrics, TGS (ordinary critical point) and TGSe (quasitricritical point). This have been done in order to (a) elucidate possible systematic deviations from asymptotic scaling, (b) investigate the metastability[5] region at $T \leqslant T_C$, and (c) to detect the presence, or lack of it, of logarithmic corrections[6] of pure scaling in the pattern displayed by the data.

In this work we present data which are substantially improved with respect to those given in previously published work.[3,4] The improvements include higher accuracy, a broader temperature range examined, and a much closer set of points giving the P vs E behavior at T very close to T_C, both above and below it. These improvements are important to investigate the evolution of scaled data away from the close vicinity of T_C, where asymptotic scaling was previously detected, and allow us to explore the metastable branch ($E<0, P>0$) of the P vs E data, not previously investigated.

II. EXPERIMENT

Samples of different thickness and areas were cut from good optical quality single crystals of TGS and TGSe grown from water solution. Symmetric and easily saturated loops were obtained with plates cleaved perpendicular to the ferroelectric b axis and electrodes with goldleaf at the main surfaces, which were about 0.5 cm^2 in surface and 1 mm in thickness. The measurements were performed on a TGS sample $0.500\ cm^2 \times 0.140\ cm$ and a TGSe sample of $0.105\ cm^2 \times 0.044\ cm$ (electrode area$\times$thickness, respectively). The temperature of the sample was controlled using a temperature controller (Unipan 680) capable of producing very slow linear heating and cooling ramps (~ 1 K/h in our case). Hysteresis loops were obtained using a Diament-Drench-Pepinsky[7] (DDP) circuit, with phase compensation only through change of auxiliary resistance. The loops were recorded in a relatively wide temperature interval encompassing T_C for both crystals [T_C(TGS) $=(321.470 \pm 0.005)$ K, T_C(TGSe)$=(294.683 \pm 0.005)$ K] (calculated from the fit to the scaling equation of state), using a digital oscilloscope (Nicolet NIC-310). For each loop, 4000 points were recorded at each temperature, which insured high resolution of the P vs E, hysteresis loops below T_C and nonlinear curves above T_C.

It may be noted that special precautions must be taken to get good quality, symmetric, hysteresis loops. Phase compensation, achieved by varying the auxiliary external resistance in the DDP circuit, must be performed as close as possible to T_C, because the resistivity of the crystal is temperature-dependent through the transition. In this way, the undesirable effects on $P_s(T)$ and $E_c(T)$ due to undercompensation or overcompensation can be minimized. The small asymmetry present in most loops, resulting from the small bias due to inhomogeneous distribution of charged im-



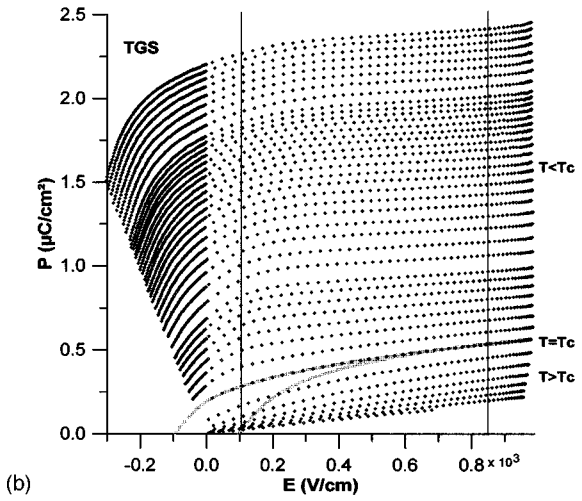
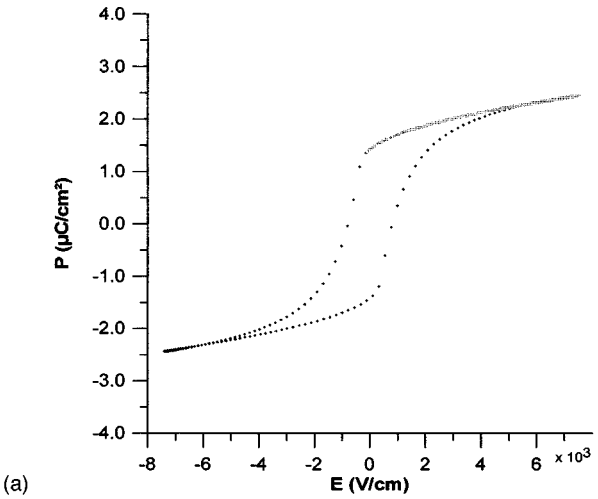


FIG. 1. (a) Digital hysteresis loop for TGS just below the transition. Thicker line shows the points from each loop that are shown in (b) and are used as raw data in what follows. (b) P (polarization) vs E (field) at various temperatures close to T_C, for triglycine sulfate (TGS) at 307 K$\leqslant T\leqslant$323 K. Only 10% the experimental points at each temperature are shown. Only one fourth of the recorded temperatures are shown for clarity of presentation. Vertical lines indicate intervening regions in which the data are little affected either by rounding effects or imperfect phase compensation (see text).



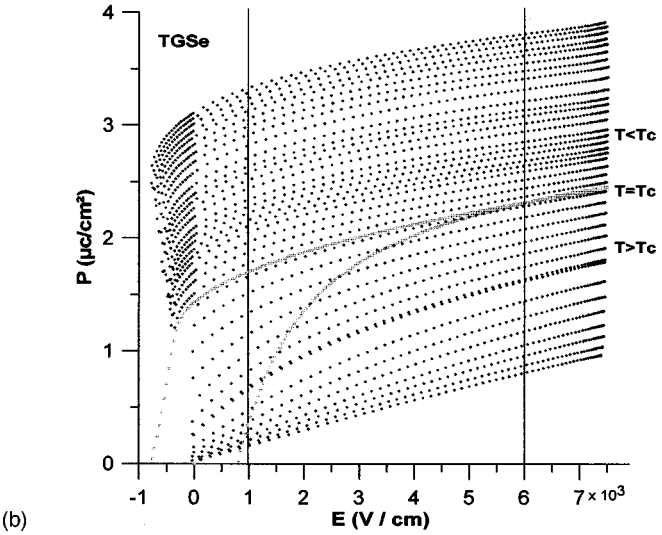


FIG. 2. (a) Digital hysteresis loop for TGSe just below the transition. Thicker line shows again the points from each loop that are shown in (b) and are used as raw data in what follows. (b) P (polarization) vs E (field) at various temperatures close to T_C, triglycine selenate (TGSe), at 284 K$\leqslant T\leqslant$298 K. Only 10% of the experimental points at each temperature are shown. Only one fourth of the recorded temperatures are shown for clarity of presentation. Vertical lines indicate intervening regions in which data are little affected either by rounding effects or imperfect phase compensation (see text).

purities, should be taken care of, first, by annealing the sample for 20 h at $T=70$ °C, well above T_C, and second, by shifting the center of the loop to the true center of symmetry. This was achieved with a simple iterative computer program to ensure that $|+E_c|=|-E_c|$, $|+P_s|=|-P_s|$, with P_s and E_c the spontaneous polarization and the coercive field, respectively. Also important is the choice of frequency for the driving field, which should be low (to approach equilibrium conditions) but not too low in order to avoid excess ionic conduction. We have used a frequency around 50 Hz for most measurements. The final, but very important factor, is the unavoidable thermal gradient from the lower to upper surface of the sample that must be minimized. The estimation of this gradient for our experimental setup gave the value of $\sim$0.01 K/cm.

III. RESULTS

Figures 1(a) and 2(a) show typical hysteresis loops for TGS and TGSe in the vicinity of the transition. Thicker lines point which part from each loop is taken to plot Fig. 1(b) and Fig. 2(b), which show the set of $P(E)$ below and above T_C, for TGS and TGSe, respectively. The $P(E)$ values for $E<0$, down to the inflection point in P vs E correspond to metastable states. The curves corresponding to $T\approx T_C$ were determined, as shown below (Figs. 3 and 4), from $P^3(E)$ for TGS, and $P^5(E)$ for TGSe. This allowed us to identify the critical and the tricritical isotherm, respectively, through the observation of the straight lines which passes through the origin ($E=0$, $P=0$). In our opinion such plots are important

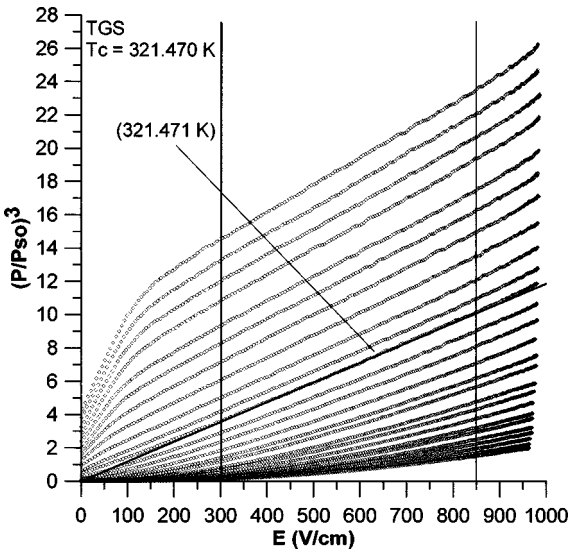


FIG. 3. Normalized polarization up to the third power (p^3) vs field (E) at various temperatures (for 321 K$\leqslant T \leqslant$322.1 K) close to T_C, defining the ordinary critical isotherm ($T=T_C=321.470$ K). The actual temperature corresponding to the experimental data (P vs E) closest to T_C is indicated. Vertical lines show the range of fields used for the linear fit of the critical isotherm.

since they give a direct, unmanipulated experimental hysteresis loop.

In Figs. 3 and 4 we present $P^3(E)$ for TGS and $P^5(E)$ for TGSe, respectively, which result in straight lines for E values higher than certain temperature-dependent threshold, and allow the identification of the critical and tricritical isotherms, respectively, which pass through the origin ($E=0$, $P=0$).

In Figs. 5 and 6 plot of P_s^2 vs T for TGS and P_s^4 vs T for TGSe, respectively, gave a linear dependence, as it is to be expected for ordinary critical and tricritical (or quasitricritical) behavior. Nevertheless the exact determination of T_c becomes somewhat more problematic in this case, because deviation from linear behavior due to the lack of perfect phase compensation in the loops.

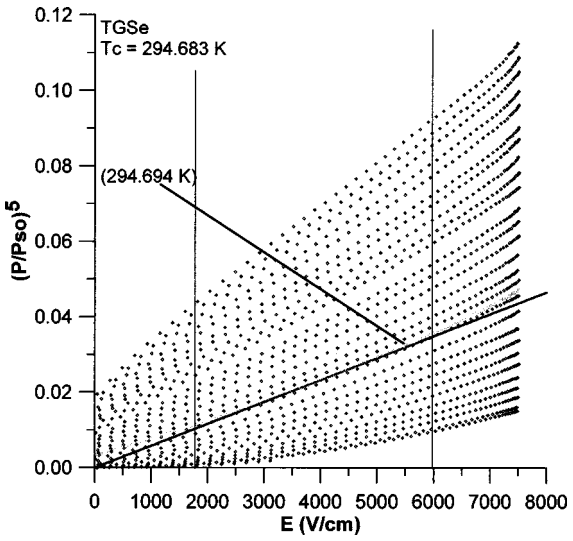


FIG. 4. Normalized polarization up to the fifth power (P^5) vs field (E) at various temperatures (283.2 K$\leqslant T \leqslant$298 K) close to T_C, defining the tricritical isotherm ($T=T_C=294.683$ K). The actual temperature corresponding to the experimental data (P vs E) closest to T_C is indicated. Vertical lines show again the range of fields used for the linear fit of the critical isotherm.

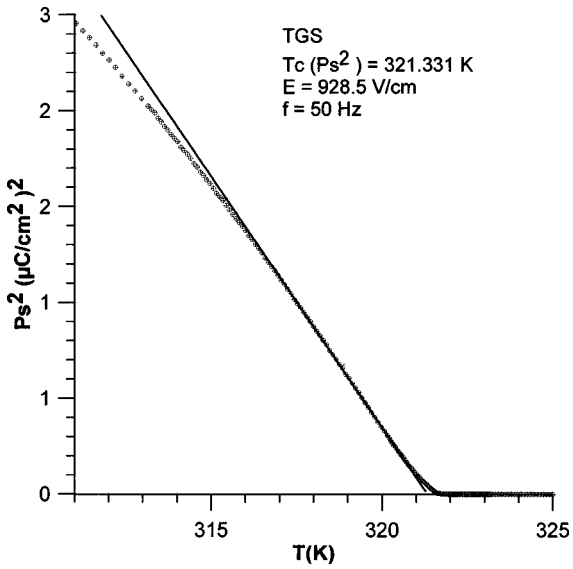


FIG. 5. Squared spontaneous polarization (P_s^2) vs T for TGS.

IV. EQUATION OF STATE

The equation of state for an uniaxial ferroelectric, which should follow a classical Landau behavior asymptotically,[3] can be extended using a generalized effective field[4] expanded in terms of odd powers of the polarization

$$E_{\text{eff}}=E+\beta_f P+\gamma_f P^3+\delta_f P^5+\cdots , \tag{1}$$

where E is the external field, P the polarization, and β_f, γ_f, δ_f are constant coefficients depending only on the geometry of the crystal lattice and the charge distribution within a unit cell.[4] For a ferroelectric crystal with N unit dipoles (μ) statistically oriented along the ferroelectric axis, with N_1 in the

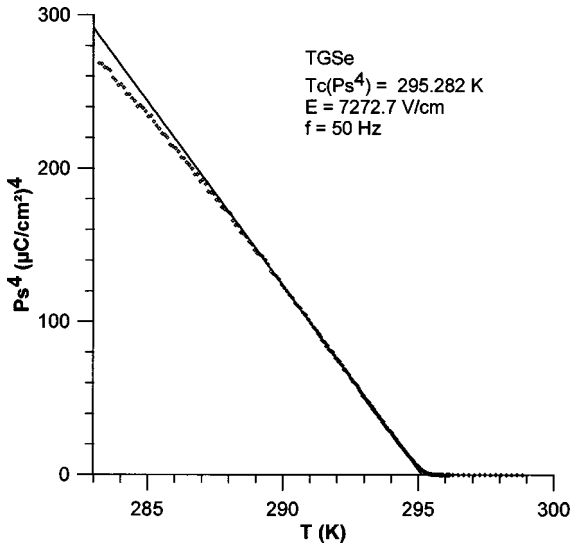


FIG. 6. Fourth power of the spontaneous polarization (P_s^4) vs T for TGSe.

direction of the field and N_2 in the opposite direction ($N_1+N_2=N$), the polarization is given[3] by

$$P=(N_2-N_1)\mu=N\mu\ \tanh\left(\frac{E_{\rm eff}\mu}{k_BT}\right), \tag{2}$$

where k_B is the Boltzmann's constant and T the temperature. From this relationship it is straightforward to get the equation of state in terms of reduced variables ($e=E/E_{s0}, E_{s0}\equiv\beta N\mu$; $p=P/P_{s0}, P_{s0}\equiv N\mu$) as

$$e=\frac{T}{T_c}\tanh^{-1}(p)-(1+gp^2+hp^4\cdots)p, \quad g=\frac{\gamma_f}{\beta_f}N^2\mu^2,$$

$$h=\frac{\delta_f}{\beta_f}N^4\mu^4 \tag{3}$$

and, expanding $\tanh^{-1}p$ in powers of p, which is especially useful for a subsequent investigation of the asymptotic equation ($e\ll1$, $p\ll1$, $(T-T_c)/T_c\ll1$), we get

$$e=\frac{T-T_c}{T_c}p+\left(\frac{1}{3}\frac{T}{T_c}-g\right)p^3+\left(\frac{1}{5}\frac{T}{T_c}-h\right)p^5\cdots \tag{4}$$

This is the general equation of state for a dipolar uniaxial ferroelectric, valid at the vicinity of ordinary as well as of quasitricritical points. It is analogous to the equation derived from Landau's theory,[5] but not identical because it contains specific temperature dependences of the coefficients of the successive powers of the polarization.

For TGS (ordinary critical point, $g<\frac{1}{3}$) Eq. (4) can be written in the scaling form as

$$\hat{e}=\pm\hat{p}+\left\{\left(\frac{1}{3}\frac{T}{T_c}-g\right)+\Phi_c\left[(T-T_c)/T_c,\hat{p}\right]\right\}\hat{p}^3, \tag{5}$$

where $\hat{e}\equiv e/|(T-T_c)/T_c|^{3/2}$, $\hat{p}\equiv p/|(T-T_c)/T_c|^{1/2}$ are the scaled variables, and

$$\Phi_c[(T-T_c)/T_c,\hat{p}]\equiv\left\{\frac{1}{3}\left(\frac{T-T_c}{T_c}\right)\pm\left[\left(\frac{1}{5}-g\right)\left(\frac{T-T_c}{T_c}\right)+\frac{1}{5}\left(\frac{T-T_c}{T_c}\right)\right]\hat{p}+\cdots\right\} \tag{6}$$

In Eq. (5) the $\pm$ signs correspond to the $T>T_c$ branch and the $T<T_c$ branch, respectively, and $\Phi_c[(T-T_c)/T_c,\hat{p}]$, which becomes important only for T below and away from T_c, changes from $\Phi_c[0,\hat{p}]\to0$ at $T\approx T_c$ to $\Phi_c[-1,1]\to$const at $T\approx0$, always for $e\ll1$. It may be noted that $E_{s0}=\beta N\mu$ is in practice much larger than the breakdown field, and therefore the behavior at $e\approx1$ is not relevant experimentally.

For TGSe (quasitricritical point, $g\approx\frac{1}{3}$), on the other hand, the term in $\hat{p}^3$ disappears, and Eq. (4) should be written in scaling form as

$$\hat{e}=\pm\hat{p}+\left\{\left[\frac{1}{5}\frac{T}{T_c}-h\right]+\Phi_{tc}[(T-T_c)/T_c,\hat{p}]\right\}\hat{p}^5, \tag{7}$$

where $\hat{e}\equiv e/|(T-T_c)/T_c|^{5/4}$, $\hat{p}\equiv p/|(T-T_c)/T_c|^{1/4}$, and

$$\Phi_{tc}[(T-T_c)/T_c,\hat{p}]\equiv\left\{\frac{1}{5}\left(\frac{T-T_c}{T_c}\right)\pm\left[\left(\frac{1}{7}-k\right)\left(\frac{T-T_c}{T_c}\right)+\frac{1}{7}\left(\frac{T-T_c}{T_c}\right)\right]\hat{p}^2+\cdots\right\}. \tag{8}$$

Note that scaled variables and $\Phi_{tc}[(T-T_c)/T_c,\hat{p}]$ are now defined differently. Again, in Eq. (7) the $\pm$ signs correspond to the $T>T_c$ branch and $T<T_c$ branch, respectively, and $\Phi_{tc}[(T-T_c)/T_c,\hat{p}]$, which also becomes important only for $T<T_c$ and towards the low-temperature region, goes from $\Phi_{tc}[0,1]\to0$ at $T\approx T_c$, to $\Phi_{tc}[(-1),\hat{p}]\to$const at $T\approx0$, always for $e\ll1$.

Figure 7 gives $\ln\hat{p}$ vs $\ln\hat{e}$ for TGS, together with the asymptotic equation of state corresponding to an ordinary critical point

$$\hat{e}=\pm\hat{p}+(\tfrac{1}{3}-g)\hat{p}^3, \quad (g=0.24\pm0.05). \tag{9}$$

It can be seen that for $T<T_c$ and away from T_c, scaling still holds well, i.e., the data for different temperatures continue to collapse on a single curve, but the coefficient of $\hat{p}^3$ changes gradually as it should, towards one, marked as a dashed line in the figure, because $T\to0$, $p\to1$ ($P_s\to P_{s0}$), and $\hat{p}$ goes to unity, which results in $\ln\hat{p}$ going to zero. For $T>T_c$ the fit to the asymptotic Eq. (9) is almost perfect in the whole experimental range. It may be noted that the set of experimental points further up in the graph corresponds to a particular temperature extremely close to T_c, and that the nearest sets at both sides are substantially away form T_c, in comparison. A sequence of sets at more closely spaced temperatures would have closed the gap between neighboring set of isothermal points in the graph.

Likewise, Fig. 8 gives, for TGSe, $\ln\hat{p}$ vs $\ln\hat{e}$, where $\hat{p}$ and $\hat{e}$ are now defined in the way appropriate for tricritical point behavior, and shows the asymptotic equation of state corresponding to a tricritical point.

$$\hat{e}=\pm\hat{p}+(\tfrac{1}{5}-h)\hat{p}^5, \quad (h=0.14\pm0.05). \tag{10}$$

Also in this case the agreement between theory and experiment is good and scaling holds very well for all our data obtained for $T>T_c$. For the data obtained below T_c the deviation from the asymptotic equation is smaller than in the previous case, as expected. Note that experimental data in both cases (TGS and TGSe) collapse on the asymptotic equation of state in a wide range (more that six orders of magnitude). The coefficient of $\hat{p}^5$ changes again gradually towards one as $\hat{p}$ goes to unity with $T\to0$.

V. METASTABLE BEHAVIOR

Figures 7 (TGS) and 8 (TGSe) also include points corresponding to the metastable behavior ($E<0$, $P>0$) showed in the loops (see Figs. 1 and 2). It is well known that, due to the forward and sidewise motion of domain walls,[8] the ferroelec-

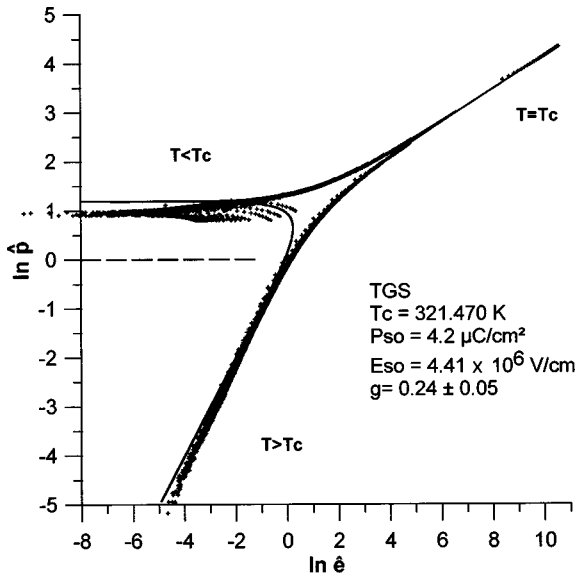


FIG. 7. Scaled data $\ln \hat{p}$ $\ln \hat{e}$, at $T<T_C$, including metastable data ($E<0$, $P>0$) and at $T>T_C$, for TGS ($307\ \mathrm{K} \leqslant T \leqslant 323\ \mathrm{K}$), where $\hat{e} \equiv e/|(T-T_c)/T_c|^{3/2}$ and $\hat{p} \equiv p/|(T-T_c)/T_c|^{1/2}$ are the scaled field and the scaled polarization, respectively. The continuous curve is the asymptotic equation of state [Eq. (9)] for an ordinary critical point. The dashed line shows the expected asymptotic behavior as $T \to 0$ K. Note that experimental data collapse on the asymptotic equation of state in a wide range (more than ten orders of magnitude in scaled field and four orders in scaled polarization).

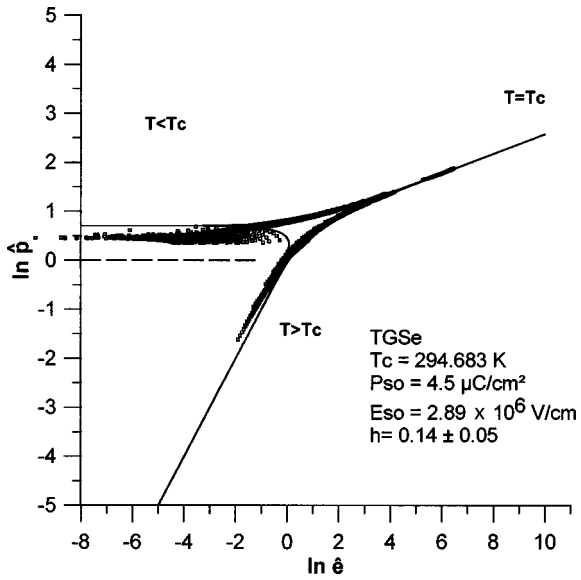


FIG. 8. Scaled data $\ln \hat{p}$ vs $\ln \hat{e}$, at $T<T_C$, including metastable data ($E<0$, $P>0$) and at $T>T_C$ for TGSe ($284\ \mathrm{K} \leqslant T \leqslant 298\ \mathrm{K}$), were $\hat{e} \equiv e/|(T-T_c)/T_c|^{5/4}$ and $\hat{p} \equiv p/|(T-T_c)/T_c|^{1/4}$ are the corresponding scaled field and scaled polarization. The continuous curve is the asymptotic equation of state [Eq. (10)] for a tricritical point. The dashed line shows the expected asymptotic behavior as $T \to 0$ K. Again, the asymptotic equation is valid in a wide range of field and polarization.

tric coercive field, which determines the metastability region, is orders of magnitude lower than the ideal (thermodynamic) coercive field. It may therefore be expected that, as T_c is approached from below, the ''contrast'' between domains decreases, the effective field at the domain boundaries approaches asymptotically to the ideal (bulk) effective field value. If this is so, we may expect that the scaled data corresponding to the metastable portions of the loops approach the metastable branches of the scaling equations,

$$-\hat{e} = -\hat{p} + (\tfrac{1}{3} - g)\hat{p}^3 \quad \text{for TGS}, \tag{11}$$

$$-\hat{e} = -\hat{p} + (\tfrac{1}{5} - h)\hat{p}^5 \quad \text{for TGSe}, \tag{12}$$

which are represented as $\ln|\hat{p}|$ vs $\ln|\hat{e}|$ in Figs. 7 and 8, returning from the left and going down. It can be seen that the shapes of the curves defined by the data are similar to those defined by Eqs. (11) and (12), and that there is a clear tendency in both sets of data to move towards the metastable branches of respective scaling equations.

VI. DISCUSSION

We may conclude that scaling holds in uniaxial ferroelectric TGS (TGSe) at points substantially further away from critical (tricritical) point than previous investigations.[3,4] Deviations from asymptotic scaling for $T<T_C$ take place, gradually, towards the expected behavior when $T \to T_C$, in accordance with analytic expression, given by Eqs. (5) and (7), obtained within a generalized effective field approach.

For points in metastable regions ($E<0$, $P>0$) the data show a clear tendency, both for TGS and TGSe, to approach the metastable branches of the corresponding scaling equations (solid line in Figs. 7 and 8).

No logarithmic corrections[6] are clearly visible in our scaled data. Such corrections (predicted a long time ago[9]) are important for uniaxial ferroelectrics but have not yet been fully elucidated experimentally by hysteresis loop measurements. This might be taken to imply that the role of fluctuations is less important in uniaxial ferroelectrics at $T \approx T_C$ than that of other nonlinear electric or elastic interactions in the crystals. Around $T_C \pm 1$ K the estimated error of polarization for a driving field amplitude is less than 3%, which sets an upper limit for possible logarithmic corrections. Nevertheless as it was previously mentioned it is quite difficult to achieve perfect phase compensated loops at $T \approx T_C$. To the best of our knowledge this is the first experimental work

TABLE I. Scaling constant for uniaxial ferroelectrics TGS and TGSe.

Crystal	T_C (K)	C (K)	P_{so} (μC/cm^2)	E_{so} (10^6 V/cm)	E_{SO}/P_{SO}	$4\pi T_C$ C	g	h
TGS	321.47	3650	4.2	4.41	1.16	1.10	0.24	
TGSe	294.68	4050	4.5	2.89	0.76	0.91	$\approx \frac{1}{3}$	0.14

exploring the metastable behavior at $T \approx T_C$ in uniaxial ferroelectrics.

Table I summarizes scaling data for TGS and for TGSe. The respective Curie constants are from previous dielectric constant measurements.[3,10,11] The consistency between $\beta = E_{s0}/P_{s0}$ and $\beta = (4\pi T_C)/C$ is much better than in the previous works.[3,4]

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