Equation of state, Debye-Waller factor, and electrical resistivity of ferroelectrics near their critical point

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The Larkin-Khmelnitskii theory of uniaxial ferroelectrics is used to derive further predictions for the critical behavior of ferroelectrics, including "local properties" and transport properties. Special attention is paid to the experimental observability of the predicted logarithmic correction terms. In particular, in the expansion of the electric field E in powers of the dielectric polarization P, i.e., $E=P\Sigma_i f_{2i}(T)P^{2i}$, the temperature dependence of the coefficients $f_2 \propto |\ln(T/T_c-1)|^{-1}$ and $f_4 \propto (T/T_c-1)^{-1}|\ln(T/T_c-1)|^{-4/3}$ is obtained, deviating significantly from $f_2=$ const and $f_4=$ const of the simple Landau theory. We argue that the nonanalytic behavior of f_2 could be measured more easily than either the logarithmic correction in $f_0 \propto (T/T_c-1)|\ln(T/T_c-1)|^{-1/3}$ or the specific-heat singularity $C \propto |\ln(T/T_c-1)|^{1/3}$. We show that recent experiments on tri-glycine sulfate by Ehses and Müser are in good agreement with our predictions. Moreover, we calculate the temperature dependence of the critical contribution to the Debye-Waller-factor exponent W which corresponds to that of the electron-paramagnetic-resonance linewidth in the "slow-motion regime." We find $W_{\rm crit} \propto (T/T_c-1) \times |\ln(T/T_c-1)|^{1/3}$ above T_c and $W_{\rm crit} \propto (1-T/T_c)|\ln(T/T_c-1)|^{2/3}$ below T_c. A reinterpretation of available experiments is suggested. Finally, we obtain the temperature dependence of the critical contributions to the dc electrical resistivity ρ both for ferroelectrics and other structural phase transitions. While $d\rho/dT$ is shown to have the same singularity as the specific heat in ferroelectrics both below T_c and above T_c we obtain in the other cases $d\rho/dT \propto (1-T/T_c)^{2\beta-1}$ for $T<T_c$, and $d\rho/dT \propto C \propto (T/T_c-1)^{-\alpha}$ for $T>T_c$, where β is the order-parameter exponent. A discussion of a recent experiment in SnTe is given, and our results for the electrical resistivity of semiconducting ferroelectrics are compared with those for ferromagnets and antiferromagnets.

I. INTRODUCTION

The basic theory of the critical behavior of uniaxial ferroelectric materials like tri-glycine sulfate (TGS), etc.[1] or anisotropic ferromagnets with dipolar interactions like $LiTbF_4$, for instance,[2,3] has received considerable recent attention.[4-9] The reason for this interest comes mainly from the renormalization-group approach[10,11] which showed that for uniaxial systems with dipolar forces the dimensionality $d=3$ is a "marginal dimensionality" d^*: i.e., for $d>d^*$ "classical" critical behavior as predicted by the Landau theory[12] of phase transitions applies, for instance, the exponents of the order parameter and the associated susceptibility are $\beta=\frac{1}{2}$ and $\gamma=1$. For $d \leq d^*$ fluctuations neglected by the Landau theory lead to a different critical behavior: For $d<d^*$ the exponents are distinctly nonclassical and scaling theory[13] applies.[14] At $d=d^*$, however, classical exponents are found together with fractional powers of logarithmic factors as multiplicative correction terms, such that simple scaling behavior does not hold.[4-9] While the renormalization-group approach rests on approximations for $d<d^*$, exact solutions of the renormalization-group equations are possible for $d=d^*$, and further details like critical amplitude ratios, etc.[9] can be worked out. Obviously, experimental studies for $d=d^*$ would be an extremely valuable check on our modern understanding[10,11] of phase transitions and critical fluctuations.

Unfortunately, for standard critical phenomena in usual magnets, fluids, critical binary mixtures, or structural phase transitions, $d^*=4$ and thus unaccessible to any experimental study.[10] Tricritical phenomena[15] where $d^*=3$, too,[16] involve a larger number of critical parameters, and thus a meaningful comparison with experiment is much harder. On the other hand uniaxial ferroelectric systems, to which the original theory of Larkin and Khmelnitskii[4] is addressed, were usually[1,17] interpreted entirely in terms of standard Landau theory[12] or its ramifications,[17] without any logarithmic corrections due to fluctuations. Thus the only experimental example where these logarithmic effects have definitively been observed[2] is the specific heat of $LiTbF_4$, while already studies of its order parameter and susceptibility gave ambiguous results,[3] as well as the measurement of specific heat[18] and thermal expansion[19] in ferroelectrics.

In view of this unsatisfactory situation, we reexamine in the present paper the critical behavior of uniaxial ferroelectrics on the basis of the Lar-

kin-Khmelnitskii theory,[4] calculating the critical singularities of *additional* properties which have not been considered so far.[4-9] In Sec. II we consider the critical singularities of the expansion coefficients of the free energy in terms of the order parameter and compare it to a recent experiment of Ehses and Müser.[20] In Sec. III we extend our previous analysis of the Debye-Waller factor at structural phase transitions[21] to derive the appropriate logarithmic correction factors. Section IV then contains a treatment of the electrical resistivity of (semiconducting) ferroelectrics, which has recently been shown experimentally[22] in SnTe to have a critical anomaly. While our starting point is similar to the theory of de Gennes and Friedel[23] and Fisher and Langer[24] for the critical electrical resistivity of magnets, our treatment allows for a simple comparative discussion of both ferroelectrics and other structural transitions and avoids pitfalls which have hampered the treatment of ferromagnets[23-25] and antiferromagnets.[26] Therefore, we present a unified treatment of these magnetic cases along similar lines in an Appendix.

II. EXPANSION COEFFICIENTS IN THE EQUATION OF STATE

Here we are concerned with the free energy $F(T,P)$ of a uniaxial ferroelectric[27] as a function of the order parameter, the dielectric polarization P in the direction of the preferred axis, in the vicinity of the critical temperature T_c. Since it is important not only to detect deviations from classical Landau theory but also to show that they are *not* of the type as predicted by a usual scaling treatment, we discuss the expansion of $F(T,P)$ in powers of P both from the point of view of scaling theory[13] and Larkin-Khmelnitskii theory.[4]

First we note, from general thermodynamics, that the electric field E (or more generally, the variable conjugate to the order parameter) is given by

$$E=\left(\frac{\partial F(T,P)}{\partial P}\right)_T, \tag{1}$$

and that E has an analytic expansion[28] in P for all temperatures $T\neq T_c$. Since we have invariance with respect to a change of sign of both E and P, this expansion reads

$$\begin{aligned} E &\equiv Pf(P^2,T) \\ &= P\sum_i f_{2i}(T)P^{2i} \\ &= P[f_0(T)+f_2(T)P^2+f_4(T)P^4+\cdots], \end{aligned} \tag{2}$$

where $f_0(T)$ is the standard inverse susceptibility and $f_2(T)$, $f_4(T)$ are the functions on which attention is focused in the present paper. Classical Landau theories require the $f_{2i}(T)$ to be analytic also in the variable (T_c-T), i.e.,

$$\begin{aligned} f_0(T) &= f_{01}(T_c-T)+\cdots, \\ f_2(T) &= f_{20}+f_{21}(T_c-T)+\cdots, \\ f_4(T) &= f_{40}+f_{41}(T_c-T)+\cdots. \end{aligned} \tag{3}$$

From these expressions it is already clear that any logarithmic corrections to the zero-field susceptibility $\chi_0\propto f_0^{-1}$ and the order parameter $\propto(-f_0/f_2)^{1/2}$ will be masked by the leading power-law critical behavior. In f_2, however, a logarithmic term would be the leading singularity, similar to the behavior of the specific heat,[4] and will thus be easier accessible by experiment.[28]

First we obtain the temperature dependence of the $f_{2i}(T)$ as it would be predicted from scaling theory.[13] In the homogeneity assumption $(\epsilon\equiv T/T_c-1)$ the most singular part of E is given by

$$E=\chi_0^{-1}P\tilde{f}(P^2\epsilon^{-2\beta}), \quad \chi_0=\hat{\chi}_0\epsilon^{-\gamma}. \tag{4}$$

We expand the scaling function

$$\tilde{f}(x)=1+(\hat{f}_2/\hat{\chi}_0)x+(\hat{f}_4/\hat{\chi}_0)x^2+\cdots$$

for small arguments to obtain, using the exponent relation[13] $\delta=1+\gamma/\beta$,

$$f_2(T)=\hat{f}_2\epsilon^{\gamma-2\beta}, \quad f_4(T)=\hat{f}_4\epsilon^{\beta(\delta-5)}. \tag{5}$$

While this treatment does not make a prediction concerning the magnitude of the critical amplitudes $\hat{\chi}_0$, $\hat{f}_2$, $\hat{f}_4$, ..., the rather generally accepted exponent estimates for three-dimensional uniaxial systems[29] $\gamma\simeq 1.25$, $\delta\simeq 4.8$, $\beta\simeq 0.32$ imply that $\chi_0^{-1}\propto\epsilon^{1.25}$, $f_2(T)\propto\epsilon^{0.61}$, $f_4(T)\propto\epsilon^{-0.06}$. Thus, drastic deviations from classical behavior are expected *both* in $f_0(T)$ and in $f_2(T)$ but *not*[30] in $f_4(T)$.

Next we derive the temperature dependence of the $f_{2i}(T)$ as it follows from Larkin-Khmelnitskii theory.[4] Rather than starting from the original approach[31] it is more convenient to use the equivalent results of Bervillier,[8] which we rewrite as follows (a, b, and g are phenomenological constants):

$$E=a(\epsilon\tilde{P}+\tfrac{1}{6}g\tilde{P}^3), \tag{6a}$$

$$\tilde{P}=bP|\ln(\epsilon+\tfrac{1}{2}ga^2P^2)|^{-1/3}. \tag{6b}$$

These equations beautifully demonstrate that the classical Landau expansion is valid only in terms of a "renormalized" order parameter $\tilde{P}$, which differs from P due to a logarithmic correction factor accounting for fluctuation effects. From Eqs. (6) we find by straightforward Taylor expansions

$$E = abP\epsilon|\ln\epsilon|^{-1/3} + \tfrac{1}{6}gabP^3|\ln\epsilon|^{-1}(b^2 + a^2|\ln\epsilon|^{-1/3}) + \tfrac{1}{12}g^2a^3bP^5(1/\epsilon)|\ln\epsilon|^{-4/3} \times (-\tfrac{1}{2}a^2 + b^2|\ln\epsilon|^{-2/3} + \tfrac{2}{3}a^2|\ln\epsilon|^{-1}) + \cdots . \quad (7)$$

From Eq. (7), one immediately obtains the standard[4] result $\chi_0^{-1} \propto \epsilon|\ln\epsilon|^{-1/3}$ and the new results, to leading order,

$$f_2(T) \propto |\ln\epsilon|^{-1} \xrightarrow[\epsilon\to 0]{} 0, \qquad f_4(T) \propto \epsilon^{-1}|\ln\epsilon|^{-4/3} \xrightarrow[\epsilon\to 0]{} \infty . \quad (8)$$

It can be shown that the inverse of the susceptibility $\chi^{-1} \equiv \partial E/\partial P$ is nonzero for $ga^2P^2/2\epsilon \ll 1$, where this expansion is valid, although the leading term of $f_4(T)$ is negative.

These findings imply that while $f_0(T)$ is hardly different from the classical Landau prediction, the deviations of $f_2(T)$ and $f_4(T)$ are clearly more pronounced, since $f_2(T)$ should go to zero at T_c rather than staying constant, while $f_4(T)$ diverges strongly. The latter prediction is also qualitatively different from Eq. (5).

It turns out that these predictions are in very good agreement with recent measurements[20] on TGS, where both $f_0(T)$ and $f_2(T)$ have been recorded for $6\times10^{-4} \lesssim \epsilon \lesssim 3\times10^{-2}$ with rather high precision, and also some qualitative features of $f_4(T)$ can be inferred.[32] These authors[20] find good agreement with the Curie-Weiss law $f_0(T) \propto \epsilon$, with a small *decrease* of the Curie constant which was fitted[20] by a power law $\epsilon^{0.02}$. Obviously, this decrease can be attributed to the $|\ln\epsilon|^{-1/3}$ correction as well. The coefficient $f_2(T)$ is fitted as[20] $\epsilon^{0.1}$, but Fig. 1 demonstrates that the data are very well consistent with the predicted $|\ln\epsilon|^{-1}$ behavior of Eq. (8). Moreover, the data on $f_2^{\rm eff}(T, P^2) = f_2(T) + f_4(T)P^2 + \cdots$ vs P^2 show that the initial slope of $f_2^{\rm eff}$ increases strongly, as T_c is approached, again in qualitative accord with Eq. (8). All these observations fit nicely in the pattern of behavior as deduced from the Larkin-Khmelnitskii theory, but are quite inconsistent with the behavior according to the scaling theory [Eq. (5)]. In Ref. 20, *ad hoc* explanations of the data have been attempted introducing additional intrinsic fields the physical origin of which seems somewhat obscure to us. Moreover, no explanation whatsoever could be given for the temperature dependence of the new parameters[33] near T_c. We feel that these *ad hoc* explanations should be abandoned, since their spirit is that the behavior of ideal ferroelectric materials should be strictly classical,[17] which is incorrect.

III. LOGARITHMIC CORRECTIONS IN THE DEBYE-WALLER FACTOR (DWF)

We consider the exponent $W_\kappa(\vec{Q})$ of the DWF for the κth sublattice of a ferroelectric. To leading order in the momentum transfer $\vec{Q}$ of the scattering, we have[34]

$$W_\kappa(\vec{Q}) \equiv -\ln\langle e^{i\vec{Q}\cdot\vec{u}(\kappa,l)}\rangle = \tfrac{1}{2}\vec{Q}\cdot\langle\vec{u}(\kappa,l)\vec{u}(\kappa,l)\rangle\cdot\vec{Q} + \cdots , \quad (9)$$

where $\vec{u}(\kappa, l)$ is the displacement operator of a lattice particle (ion) on sublattice κ in the lth unit cell. In evaluating the thermal averages $\langle\cdots\rangle$ in (9) it is convenient to separate the *spontaneous static displacements* in the cells representing the distortion to the low-temperature phase taking place at the ferroelectric ordering and the accompaning change of lattice symmetry. This may be achieved by introducing an operator $\vec{\phi}(\kappa l)$ which is measuring displacements relative to the equilibrium positions $\vec{R}(\kappa l)$ of the undistorted phase and whose expectation value $\langle\vec{\phi}(\kappa l)\rangle$ represents a static displacement, i.e.,

$$\vec{\phi}(\kappa l) = \langle\vec{\phi}(\kappa l)\rangle + \vec{u}(\kappa l) = (Nm_\kappa)^{-1/2}\sum_{\vec{q}j}\vec{e}^{\,j}(\kappa\vec{q})A^j(\vec{q})e^{i\vec{q}\cdot\vec{R}(\kappa l)} . \quad (10)$$

In (10) $\vec{e}^{\,j}(\kappa\vec{q})$ denotes the polarization vector of the jth phonon branch with wave vector $\vec{q}$, m_κ is the mass of the lattice particle at the κth sublattice. We have N unit cells and $A^j(\vec{q})$ is the phonon normal coordinate operator. Above T_c, $\langle\vec{\phi}(\kappa l)\rangle \equiv 0$, while below T_c a soft mode of polarization j_0 and wave vector[35] $\vec{q}_0$ "freezes in" giving rise to

$$\langle\vec{\phi}(\kappa l)\rangle = (Nm_\kappa)^{-1/2}\vec{e}^{\,j_0}(\kappa\vec{q}_0)\langle A^{j_0}(\vec{q}_0)\rangle e^{i\vec{q}_0\cdot\vec{R}(\kappa l)} \neq 0 . \quad (11)$$

Apart from constant factors, the macroscopic dielectric polarization P is then expressed in terms of the expectation value of the normal co-

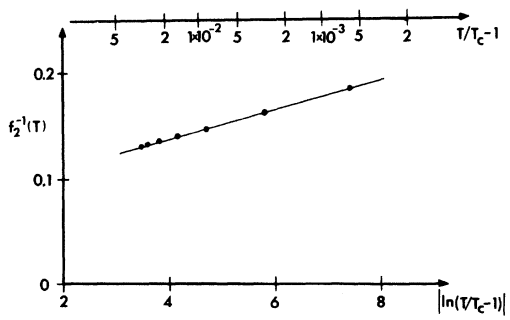

FIG. 1. Inverse expansion coefficient $f_2^{-1}(T)$ plotted vs $\ln(T/T_c - 1)$. The points are data on TGS taken from Ref. 20. While Landau theory predicts $f_2^{-1}(T)$ to be independent of T in the regime of temperatures shown, Eq. (8) predicts linear variation of $f_2^{-1}(T)$ with $\ln(T/T_c - 1)$.

ordinate operator in the limit of an infinitely large crystal by

$$P \propto N^{-1/2}\langle A^{j_0}(\vec{q}_0)\rangle . \tag{12}$$

From Eqs. (9)–(12) we note that the exponent of the DWF may be written as

$$W_\kappa(\vec{Q}) = \tfrac{1}{2}\vec{Q}\cdot[\langle\vec{\phi}(\kappa l)\vec{\phi}(\kappa l)\rangle - \langle\vec{\phi}(\kappa l)\rangle\langle\vec{\phi}(\kappa l)\rangle]\cdot\vec{Q}$$
$$= (2Nm_\kappa)^{-1}\sum_{\vec{q}j}|\vec{Q}\cdot\vec{e}^{\,j}(\kappa\vec{q})|^2 \times[\langle A^j(\vec{q})A^j(-\vec{q})\rangle - P^2\delta_{jj_0}\delta_{\vec{q},\vec{q}_0}], \tag{13a}$$

i.e., its critical part is given by the critical part of the mean-square sublattice displacements:

$$\langle\vec{u}^2\rangle_{\rm crit} \propto \sum_{\vec{q}}[\langle A^{j_0}(\vec{q})A^{j_0}(-\vec{q})\rangle - P^2\delta_{\vec{q},\vec{q}_0}]. \tag{13b}$$

Following the arguments given in our previous work,[21] the critical part of the internal energy $U = \langle\mathcal{H}\rangle = -T^2[\partial(F/T)/\partial T]_P$ is also expressed in terms of a correlation function bilinear in the normal coordinates of the j_0th phonon branch:

$$\langle\mathcal{H}\rangle_{\rm crit} = \sum_{\vec{q}} v^{\rm eff}(\vec{q})\langle A^{j_0}(\vec{q})A^{j_0}(-\vec{q})\rangle . \tag{14}$$

It is important to note that the effective potential $v^{\rm eff}(\vec{q})$ is nonsingular as a function of ϵ. The singular behavior of both the specific heat and the DWF exponent arises from the behavior of the correlation function in the regime of small $K = |\vec{q} - \vec{q}_0|$. Hence it is legitimate to approximate Eqs. (13b) and (14) in replacing the summations by integrations over q up to some cutoff, $K < q_c$. Since the main contribution to the integrals does not come from the limit $K \to 0$ but comes from the vicinity of the cutoff, we may replace $v^{\rm eff}(\vec{q})$ by $v^{\rm eff}(\vec{q}_c)$, noting that $v^{\rm eff}(\vec{q}_c) \neq 0$ and $v^{\rm eff}(\vec{q})$ varies only slowly[35] with q in the vicinity of q_c. Hence the critical singularities of both quantities are still described correctly by

$$\langle\vec{u}^2\rangle_{\rm crit} \propto \int d^3q\,[\langle A^{j_0}(\vec{q})A^{j_0}(-\vec{q})\rangle - P^2\delta(\vec{q}-\vec{q}_0)], \tag{15a}$$

$$\langle\mathcal{H}\rangle_{\rm crit} \propto v^{\rm eff}(q_c)\int d^3q\,\langle A^{j_0}(\vec{q})A^{j_0}(-\vec{q})\rangle , \tag{15b}$$

i.e., the leading singularity of the DWF may be related[21] to the critical behavior of the internal energy U and the order parameter P. From the renormalization-group calculation[7]

$$F_{\rm crit}(T, P=0) = -\tfrac{3}{2}a^2\epsilon^2|\tfrac{1}{2}\ln\epsilon|^{1/3} \tag{16a}$$

and the Larkin-Khmelnitskii approach[4]

$$P_{\rm crit} \propto (-\epsilon)^{1/2}|\ln(-\epsilon)|^{1/3}, \tag{16b}$$

combined with Eqs. (15), it readily follows that the DWF singularity of an uniaxial ferroelectric is given by

$$\langle\vec{u}^2\rangle_{\rm crit} = \langle\vec{u}^2\rangle_{T_c} - C_1\epsilon|\ln\epsilon|^{1/3} \quad \text{for } T > T_c, \tag{17a}$$

$$\langle\vec{u}^2\rangle_{\rm crit} = \langle\vec{u}^2\rangle_{T_c} + C_2\epsilon|\ln(-\epsilon)|^{2/3} \quad \text{for } T < T_c, \tag{17b}$$

where $\langle\vec{u}^2\rangle_{T_c}$, C_1 and C_2 are positive constants. Equations (17) describe a cusp, whose temperature dependence will resemble a linear variation with ϵ near T_c (but different slope above and below T_c) very closely. Measurements on[36] ferroelectric $Ge_xSn_{1-x}Te$ and[37] $BaTiO_3$ which seemed to give more pronounced singularities have to be considered with great precaution, however. More recent work on[38] $BaTiO_3$ and[39] $SrTiO_3$ (where the exponent of the anomaly below T_c yields a much more rapid variation with temperature[21]) failed to exhibit these critical singularities. Since one must expect[21] that $C_{1,2}/\langle\vec{u}^2\rangle_{T_c} \ll 1$ and numerous sources of error have to be considered[39] in the analysis of experimental data on the DWF, it seems unlikely to us that one can obtain the logarithmic corrections in Eqs. (17) experimentally. The same pessimism applies to the critical contribution of the isomer shift, which is expected[40] to vary $\propto\langle\mathcal{H}\rangle_{\rm crit}$ both below and above T_c, as well as to the EPR linewidth in the "slow-motion regime," whose critical temperature dependence is identical to the behavior of the DWF.[21]

IV. RESISTIVE ANOMALIES AT STRUCTURAL PHASE TRANSITIONS

Our discussion of the electrical resistivity at structural phase transitions may conveniently be based on a somewhat more general formula for the resistivity tensor[26] $\rho_{\alpha\beta}$ expressed in terms of a two-point correlation function of time derivatives $\dot{J}_\beta$ and $\dot{J}_\alpha$ of current operators ($\alpha, \beta = 1, 2, 3$):

$$\rho_{\alpha\beta} = \frac{1}{k_BT}\left(\frac{m}{e^2n}\right)^2 \lim_{z\to 0}{\rm Re}\int_0^\infty dt\, e^{izt}\int_0^{1/k_BT} d\lambda\,\langle\dot{J}_\beta(0)\dot{J}_\alpha(t+i\hbar\lambda)\rangle \to \frac{m_{\rm eff}}{e^2n_{\rm eff}\tau}, \tag{18}$$

(Im$z > 0$) being interpreted, however, analogous to the elementary relaxation-time expression.[41] Therefore, on the right-hand side of Eq. (18), e is the effective charge of the carriers, $m_{\rm eff}$ is their effective mass, and τ^{-1} denotes the scattering rate from phonons, defects, etc. Anomalies in the electrical resistivity of semiconducting ferroelectrics (or antiferroelectrics, etc.) may

arise from two sources:

(i) The new lattice periodicity below T_c which causes superzone gaps in the electronic band structure may lead to a reduction in the effective number of carriers $n_{\rm eff}$ as compared to its value in the disordered phase n_D, and hence may imply an increase of the resistivity. In the case of ferro- and antiferromagnets and order-disorder transitions it was predicted that[42,43]

$$n_{\rm eff} = n_D[1 - \hat{n}(-\epsilon)^{\beta}], \quad T \leq T_c \tag{19a}$$

while taking into account thermal smearing of the electronic band gap[44] would lead to[43,45]

$$n_{\rm eff} = n_D[1 - \hat{n}'(-\epsilon)^{2\beta}], \quad T \leq T_c \tag{19b}$$

where $\hat{n}$ and $\hat{n}'$ are constants. We expect that a behavior similar to Eq. (19b) may occur as well in a ferroelectric.

(ii) Owing to the soft phonon mode (s) a critical anomaly occurs in τ^{-1}. It is this second effect which we will consider here in more detail.

The scattering rate $\tau_{\rm ph}^{-1}$ of carriers (e.g., electrons) from phonons may be obtained according to Eq. (18) by first determining the time derivative of the electron current density operator, i.e.,

$$J_\alpha(\vec{r}) = \frac{\hbar}{2mi}\left[\psi^\dagger(\vec{r})\left(\frac{\partial\psi(\vec{r})}{\partial r_\alpha}\right) - \left(\frac{\partial\psi^\dagger(\vec{r})}{\partial r_\alpha}\right)\psi(\vec{r})\right],$$

from the corresponding equation of motion, i.e.,

$$i\hbar\dot{J}_\alpha(\vec{r}t) = [J_\alpha(\vec{r}t), H_{e-\rm ph}].$$

To this end, we approximate the Hamilton operator of the electron-ion interaction by the well-known Hamiltonian describing the electron-phonon interaction[46]:

$$H_{e-\rm ph} = -\int d^3r \sum_{l\kappa}\left(\frac{\partial V}{\partial[\vec{r} - \vec{R}(l\kappa)]}\right)\cdot\vec{u}(l\kappa)\psi^\dagger(\vec{r})\psi(\vec{r}). \tag{20a}$$

Here $V(\vec{r} - \vec{R})$ denotes the effective interaction potential between an ion at $\vec{R}$ and an electron at $\vec{r}$, and $\psi^\dagger(\vec{r})$ [$\psi(\vec{r})$] is the electron creation (annihilation) operator.[47] Thus the interaction potential $V_{e-\rm ph}$ between a single electron at site $\vec{r}$ and the displacement field $\vec{u}(l\kappa)$ reads

$$V_{e-\rm ph}(\vec{r}) = -\sum_{l\kappa}\left(\frac{\partial V}{\partial[\vec{r} - \vec{R}(l\kappa)]}\right)\cdot\vec{u}(l\kappa). \tag{20b}$$

Evaluating then the correlation-function expression of (18) further in the first Born approximation amounts to calculating the double-differential cross section for the electron-phonon scattering. Thus, we calculate matrix elements of (20b) in the first Born approximation, treating the electrons as free, restricting only their momentum $\vec{k}$ to lie within the Fermi sphere ($k < k_F$). Introducing the Fourier transform $V(\vec{q})$ of the potential $V(\vec{r} - \vec{R})$

$$V(\vec{q}) \equiv \int d^3r' e^{-i\vec{q}\cdot\vec{r}'} V(\vec{r}'), \tag{21}$$

we obtain

$$\langle\vec{k}|V_{e-\rm ph}|\vec{k}'\rangle = -i\,\vec{u}(\vec{q})\cdot\vec{q}\,V(\vec{q}), \tag{22}$$

where $\vec{q} = \vec{k} - \vec{k}'$ is the momentum transfer of the scattered electrons, and we have used the abbreviation

$$\vec{u}(\vec{q}) \equiv \sum_\kappa (Nm_\kappa)^{-1/2}\sum_j \vec{e}^{\,j}(\kappa\vec{q})A^j(\vec{q}).$$

The double-differential cross section then reads

$$\frac{d^2\sigma}{d\omega\,d\Omega} = \frac{k'}{k}\left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2 |V(\vec{q})|^2 \sum_{if}\langle i|\vec{u}(\vec{q})\cdot\vec{q}|f\rangle\langle f|\vec{u}^*(\vec{q})\cdot\vec{q}|i\rangle p_i\,\delta(\omega + (\epsilon_i - \epsilon_f)/\hbar), \tag{23}$$

where $\hbar\omega$ is the energy transfer in the scattering, $|i\rangle$, $|f\rangle$ denote initial and final state of the phonon system, ϵ_i and ϵ_f the respective energies, and p_i is the thermal occupation number. In practice only electrons with $k \simeq k_F$ contribute significantly to the scattering, and therefore the quasielastic approximation $k' \simeq k$ is appropriate, which yields [note $\vec{u}^*(\vec{q}) = \vec{u}(-\vec{q})$]

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2 |V(\vec{q})|^2 \sum_i p_i\langle i|[\vec{u}(\vec{q})\cdot\vec{q}][\vec{u}(-\vec{q})\cdot\vec{q}]|i\rangle, \tag{24a}$$

which may be written as

$$\frac{d\sigma}{d\Omega} = \left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2 |V(\vec{q})|^2 \sum_{j\kappa}(Nm_\kappa)^{-1}|\vec{q}\cdot\vec{e}^{\,j}(\kappa\vec{q})|^2[\langle A^j(\vec{q})A^j(-\vec{q})\rangle - P^2\delta_{jj_0}\delta_{\vec{q},\vec{q}_0}]. \tag{24b}$$

Now the electrical resistivity [Eq. (18)] can be found in terms of $d\sigma/d\Omega$ as[23,26]

$$\rho = \frac{m_{\rm eff}}{e^2 n_{\rm eff}^\tau} = \frac{m_{\rm eff}}{e^2 n_{\rm eff}} N\frac{\hbar k_F}{m_{\rm eff}}\int d\Omega\,(1 - \cos\theta)\frac{d\sigma}{d\Omega}, \tag{25}$$

where the scattering angle is $\Omega = (\theta, \phi)$. In the quasielastic approximation we have $\sin\theta = q/k_F$, $d\theta = dq/k_F$, $0 < q < 2k_F$, $1 - \cos\theta \approx \frac{1}{2}(q/k_F)^2$, and hence

$$\rho = \frac{\hbar k_F}{e^2 n_{\text{eff}}} \left(\frac{m_{\text{eff}}}{2\pi\hbar^2}\right)^2 \pi \int_0^{2k_F} \frac{q^3 dq}{k_F^4} |V(\vec{q})|^2 \times \sum_{j\kappa} |\vec{q}\cdot\vec{e}^{\,j}(\vec{q}\kappa)|^2 [\langle A^j(\vec{q}) A^j(-\vec{q})\rangle - P^2 \delta_{jj_0} \delta(\vec{q}-\vec{q}_0)] . \tag{26a}$$

In order to make the similarity of Eq. (26a) and Eqs. (15) as transparent as possible, we rewrite Eq. (26a) as follows:

$$\rho_{\text{crit}} \propto n_{\text{eff}}^{-1} \int d^3q\, q^3 |V(\vec{q})|^2 [\langle A^{j_0}(\vec{q}) A^{j_0}(-\vec{q})\rangle - P^2 \delta(\vec{q}-\vec{q}_0)] . \tag{26b}$$

In a simple ferroelectric, $\vec{q}_0 = 0$ and the q^3 contribution of the integrand eliminates the contribution proportional to P^2 below T_c. The dominating contributions of Eq. (26b) are then of the same type as Eq. (14) and hence[48]

$$\rho_{\text{crit}} \propto |\epsilon|\,||\ln|\epsilon||^{1/3} \quad \text{both at } T<T_c \text{ and } T>T_c, \tag{27}$$

disregarding a possible stronger temperature dependence due to n_{eff}^{-1} [Eq. (19)]. The situation is different in an antiferroelectric with $\vec{q}_0 \neq 0$, however, where the contribution proportional to the order parameter is not canceled, since then Eq. (26b) may be reduced to

$$\rho_{\text{crit}} \propto n_{\text{eff}}^{-1} |V(\vec{q}_0)|^2 q_0^3 \times \int d^3q\, [\langle A^{j_0}(\vec{q}) A^{j_0}(-\vec{q})\rangle - P^2 \delta(\vec{q}-\vec{q}_0)] , \tag{28}$$

since the critical contributions come from the region where $\vec{K} = \vec{q} - \vec{q}_0$ is very small. There we may use the expansion[49] ($\xi \propto |\epsilon|^{-\nu}$)

$$\langle A^{j_0}(\vec{q}) A^{j_0}(-\vec{q})\rangle = C_0 K^{-2+\eta} + C_1 (K\xi)^{-(1-\alpha)/\nu} \operatorname{sgn}(1 - T/T_c) + \cdots, \quad K\xi \gg 1 \tag{29}$$

where ν is the critical exponent of the correlation length ξ, and η describes the decay of correlation at T_c. The leading term of Eq. (29) gives rise to a constant, when one works out the integration in Eq. (28); this constant depends on the cutoff q_c,[48] and can thus not be obtained reliably. The next term gives rise to a $|\epsilon|^{1-\alpha}$ singularity both above and below T_c. While above T_c this is the leading singularity, the term proportional to $P^2 \propto (-\epsilon)^{2\beta}$ is more singular below T_c for $T \to T_c$ and hence we find

$$\frac{d\rho_{\text{crit}}}{dT} \propto \epsilon^{-\alpha}, \quad T > T_c \tag{30a}$$

$$\frac{d\rho_{\text{crit}}}{dT} \propto (-\epsilon)^{2\beta-1}, \quad T < T_c . \tag{30b}$$

A critical anomaly in the electrical resistivity has recently been found in the ferroelectric[22] SnTe. These authors[22] assumed that the anomaly should be described by $\rho_{\text{crit}} \propto |\epsilon|^{-1}$, which would be a much stronger singularity than that of our Eq. (27). Inspection of the raw data (Fig. 1 of Ref. 22) readily shows, that ρ obviously does *not* diverge at T_c, but has a rather small cusp there only, as predicted by Eq. (27). It is unclear to us if the accuracy of the presently available data[22] is sufficient for a more quantitative comparison, however. In view of the fact that the similarly weak anomalies at magnetic transitions (cf. Appendix) have found extensive experimental attention[50] and high-precision techniques for resistance measurements are available, similar careful work in ferro- and antiferroelectrics is suggested.

Finally we consider structural transitions where a transverse acoustic mode goes soft at $\vec{q} = 0$. Then Eq. (29) and (26b) yield

$$\frac{d\rho_{\text{crit}}}{dT} \propto |\epsilon|^{-\alpha}, \quad T \gtrless T_c . \tag{31}$$

V. CONCLUSIONS

In the present investigation, we have emphasized the fact that the Larkin-Khmelnitskii theory of uniaxial *ferroelectrics* is very important for the general theory of phase transitions and critical fluctuations, and hence a comparison between theory and experiment is highly desirable. Previous work, which was directed towards detecting the logarithmic corrections to Landau theory in the specific heat [$\propto |\ln|\epsilon||^{1/3}$], the susceptibility [$\propto |\epsilon|^{-1} |\ln|\epsilon||^{1/3}$], and the order parameter [$\propto (-\epsilon)^{1/2} |\ln(-\epsilon)|^{1/3}$], has been inconclusive, however. Therefore, we consider other quantities which may exhibit critical anomalies at T_c, like higher expansion coefficients in the equation of state, Debye-Waller factor, and electrical resistivity, and calculate the corresponding logarithmic correction terms. We point out that the most promising "candidate" for seeing such an anomaly is the expansion coefficient $f_2(T) \propto |\ln\epsilon|^{-1}$ in the expansion $E = P[f_0(T) + f_2(T) P^2 + \cdots]$, for

several reasons:

(i) In Landau theory, $f_2 = \text{const}$ similar to the specific heat. Hence it suffices to find the *leading* critical behavior, in contrast to susceptibility or order parameter.

(ii) The power of the logarithm is three times larger than in the specific heat, and hence the effect must be visible over a much more extended temperature interval. This fact is important since in real crystals rounding phenomena due to imperfections, etc. always occur which may obscure the singularity in the specific heat.

(iii) While in the specific heat the large background due to ordinary lattice vibrations at the rather high critical temperature—in contrast to the magnetic case, where an anomaly was actually observed[3]—makes measurements difficult, there are no such background problems in dielectric measurements.

Moreover, we point out that an experiment which exhibits this anomaly exists already, and reanalyzing the data of Ehses and Müser on TGS we obtain good agreement with our predictions. Studying also the behavior of $f_0(T)$ and $f_4(T)$, we find at least qualitative agreement, while the data can hardly be accounted for either by conventional Landau theory or by scaling theory.

We then proceed to obtain the critical contribution to the exponent of the Debye-Waller factor (as well as to the EPR linewidth in the slow motion regime) as being given by

$$\frac{d\langle\vec{u}^2\rangle_{\text{crit}}}{dT} \propto |\ln\epsilon|^{1/3} \quad \text{for } T > T_c ,$$

and by

$$\frac{d\langle\vec{u}^2\rangle_{\text{crit}}}{dT} \propto |\ln(-\epsilon)|^{2/3} \quad \text{for } T < T_c .$$

Since the accuracy of existing measurements is not very high, and can hardly be improved substantially due to various intrinsic difficulties, it is not possible to take reliable temperature derivatives, however.

We finally develop a general theory for critical anomalies in the electrical resistivity, generalizing also earlier approaches at magnetic transitions, pointing out errors inherent in the earlier work (cf. Appendix). While the anomaly which we predict is of very weak nature similar to that of the exponent of the DWF ($d\rho/dT \propto |\ln|\epsilon||^{1/3}$ both for $T > T_c$ and $T < T_c$ in a ferroelectric, whereas $d\rho/dT \propto \epsilon^{-\alpha}$ above T_c and $d\rho/dT \propto \epsilon^{2\beta-1}$ below T_c at other structural transitions), we argue that high-precision techniques should allow for taking temperature derivatives in this case, and show that measurements by Kobayashi *et al.* are in qualitative accord with the theory. Further measurements are suggested.

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APPENDIX: RESISTIVE ANOMALIES AT MAGNETIC PHASE TRANSITIONS

In order to assess the validity of our treatment of the electrical resistivity of ferroelectrics in Sec. IV, it is important to apply it in analogous manner to the case of magnetic transitions, where an extensive literature already exists.[23-26,50] Furthermore, our approach enables us to clarify some of the contradictory or erroneous results obtained there.[23-26]

Following de Gennes and Friedel,[23] we assume a contact interaction between the electrons of the conduction band and the spins $\vec{S}(l,\kappa)$ which contribute to the magnetic ordering,

$$H_{e\text{-}s} = -\int d^3r G \sum_{l\kappa} \delta(\vec{r} - \vec{R}(l\kappa)) \times \vec{S}(l\kappa)\cdot\psi_s^{\dagger}(\vec{r})\vec{\sigma}_{ss'}\psi_{s'}(\vec{r}) , \quad \text{(A1)}$$

where G is a coupling constant and $\vec{S}_e(\vec{r}) \equiv \psi_s^{\dagger}(\vec{r})\vec{\sigma}_{ss'}\psi_{s'}(\vec{r})$ the spin density operator of the conduction electrons [$\vec{S}_e \equiv (\vec{\sigma}_{ss'})$: Pauli spin matrices]. Scattering of electrons is then caused by the potential

$$V_{e\text{-}s}(\vec{r}) = -G \sum_{l\kappa} \delta(\vec{r} - \vec{R}(l\kappa)) \times [\vec{S}(l\kappa) - \langle\vec{S}(l\kappa)\rangle]\cdot\vec{S}_e , \quad \text{(A2)}$$

the Fourier transform of which is simply $[\delta\vec{S}(l\kappa) \equiv \vec{S}(l\kappa) - \langle\vec{S}(l\kappa)\rangle]$:

$$\langle\vec{k}|V_{e\text{-}s}|\vec{k}'\rangle = -G \sum_{l\kappa} \delta\vec{S}(l\kappa)\cdot\vec{S}_e e^{i\vec{q}\cdot\vec{R}(l\kappa)} \quad \text{(A3)}$$

and the result analogous to Eq. (23) thus reads

$$\frac{d^2\sigma}{d\omega d\Omega} = \frac{k'}{k}\left(\frac{m_{\text{eff}}}{2\pi\hbar^2}\right)^2 G^2 \sum_{if} \langle i|\sum_{l\kappa}\delta\vec{S}(l\kappa)\cdot\vec{S}_e e^{-i\vec{q}\cdot\vec{R}}|f\rangle\langle f|\sum_{l\kappa}\delta\vec{S}(l\kappa)\cdot\vec{S}_e e^{i\vec{q}\cdot\vec{R}}|i\rangle\delta\left(\omega + \frac{\epsilon_i - \epsilon_f}{\hbar}\right), \quad \text{(A4)}$$

where $|i\rangle$, $|f\rangle$ now also contain electronic spin states. In quasielastic approximation we find, performing

the trace over the electronic spin states:

$$\frac{d\sigma}{d\Omega}=\left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2 G^2 \sum_{l\kappa}\left[\langle\vec{S}(00)\cdot\vec{S}(l\kappa)\rangle-\langle\vec{S}(00)\rangle\cdot\langle\vec{S}(l\kappa)\rangle\right]e^{i\vec{q}\cdot\vec{R}(l\kappa)} \tag{A5a}$$

which may also be written as {the order parameter in this case is $\vec{M}=\sum_{l\kappa}\langle\vec{S}(l\kappa)\rangle\exp[i\vec{q}_0\cdot\vec{R}(l\kappa)]$}

$$\frac{d\sigma}{d\Omega}=\left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2 G^2[\langle\vec{S}(\vec{q})\cdot\vec{S}(-\vec{q})\rangle-M^2\delta_{\vec{q},\vec{q}_0}], \tag{A5b}$$

which has the same structure as Eq. (24b). The subsequent result for the electrical resisitivity is

$$\rho=\frac{N\hbar k_F}{e^2 n_{\rm eff}}\left(\frac{m_{\rm eff}}{2\pi\hbar^2}\right)^2\pi\int_0^{2k_F}\frac{q^3dq}{k_F^4}\,G^2[\langle\vec{S}(\vec{q})\cdot\vec{S}(-\vec{q})\rangle-M^2\delta(\vec{q}-\vec{q}_0)], \tag{A6a}$$

and hence

$$\rho_{\rm crit}\propto n_{\rm eff}^{-1}\int d^3q\,q[\langle\vec{S}(\vec{q})\cdot\vec{S}(-\vec{q})\rangle-M^2\delta(\vec{q}-\vec{q}_0)]. \tag{A6b}$$

In full analogy with Eq. (29) we have[49] [$\vec{K}=\vec{q}-\vec{q}_0$]

$$\langle\vec{S}(\vec{q})\cdot\vec{S}(-\vec{q})\rangle=C_0K^{-2+\eta}+C_1(K\xi)^{-(1-\alpha)/\nu}{\rm sgn}(1-T/T_c)+\cdots, \quad K\xi\gg1. \tag{A7}$$

In a ferromagnet $\vec{q}_0=0$, hence the extra q term in Eq. (A6b) cancels the contribution proportional to M^2, and we have

$$d\rho_{\rm crit}/dT\propto|\epsilon|^{-\alpha}\ \text{ for both } T>T_c \text{ and } T<T_c. \tag{A8}$$

This result has been obtained earlier,[25] but our derivation shows in a much simpler fashion why the conjecture of Fisher and Langer[24] that $d\rho_{\rm crit}/dT\propto(-\epsilon)^{2\beta-1}$ below T_c is incorrect. Above T_c Eq. (A8) agrees also with Ref. 24, of course.

In an antiferromagnet where $\vec{q}_0\neq0$, the extra q term in Eq. (A6b) is nonzero at $\vec{q}_0$ and thus cannot cancel the contribution proportional to M^2, and hence we obtain our asymmetric result, Eqs. (30). Equation (30b) agrees with the result of Suezaki and Mori,[26] while these authors predict $d\rho_{\rm crit}/dT\propto\epsilon^{2\beta-1}$ also above T_c, which is incorrect. The reason for this failure is that these authors extend the integrations over q to infinity instead of taking a finite cutoff q_c, although the main contribution does not come from the regime $q\xi\simeq1$ but rather from the vicinity of the cutoff. Through this algebraic error too strong a singularity is obtained, similar to various treatments of the DWF discussed in Ref. 21. We conclude by stating that our derivation clearly shows that both ρ ($T=T_c$) as well as the critical amplitude of ρ [i.e., the constant of proportionality in Eqs. (27) or (30) or (A8)] are cutoff-dependent, and hence *cannot* be estimated reliably by our present method.

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