Debye-Waller factor, compressibility sum rule, and central peak at structural phase transitions*

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The temperature dependence of the Debye-Waller factor (DWF) near the critical point of ferroelectrics, "antiferroelectrics," $A15$ structure compounds, etc., is investigated. Using the compressibility sum rule it is shown that the critical part of the DWF exponent quadratic in the momentum transfer is rigorously determined by the renormalized static phonon frequencies and thus will not be directly affected by the occurrence of a central peak. It is found that the mean-square particle displacement has a cusp at T_c, rather than the critical divergence predicted by various authors. The critical exponents associated with the cusp are estimated from scaling arguments and related to those of the specific heat. The extent to which this cusp-shaped anomaly might be detected experimentally is briefly discussed. The results obtained here are also relevant for the electron-paramagnetic-resonance linewidth in the "slow-motion" regime.

I. INTRODUCTION

In considering Mössbauer-fraction experiments or Bragg-peak intensities of x rays and neutrons being scattered from crystals, one has to deal with the well-known Debye-Waller factor (DWF) for the κth sublattice of a crystalline structure:

$$d_\kappa(\vec{Q}) = e^{-W_\kappa(\vec{Q})}$$

at a momentum transfer $\vec{Q}$. The exponent of $d_\kappa(\vec{Q})$ follows from its definition[1]:

$$W_\kappa(\vec{Q}) \equiv -\ln\langle e^{i\vec{Q}\cdot\vec{u}}\rangle = \sum_{\nu=1}^{\infty}(-i^\nu/\nu!)\langle(\vec{Q}\cdot\vec{u})^\nu\rangle_c \,. \quad (1)$$

The scalar products $\langle(\vec{Q}\cdot\vec{u})^\nu\rangle_c$ in the cumulant expansion on the right-hand side of (1) involve successively higher powers of momentum transfers $\vec{Q}^\nu$ and higher-order lattice-particle displacement correlation functions or cumulants[2] $\langle\vec{u}^\nu\rangle_c$ of displacement operators $\vec{u}(\kappa\vec{l})$ of the κth lattice particle in the $\vec{l}$th unit cell, giving rise to a first nonvanishing term:

$$W_\kappa(\vec{Q}) = \tfrac{1}{2}\vec{Q}\cdot\langle\vec{u}(\kappa\vec{l})\vec{u}(\kappa\vec{l})\rangle\cdot\vec{Q} + \cdots \,.$$

At second-order structural phase transitions the ordering involves spontaneous shifts of lattice particles to new equilibrium positions within the unit cell which, in the low-temperature phase, may or may not be enlarged by the resulting static distortion depending on the system. Thus, one expects $W_\kappa(\vec{Q})$ to be rather directly affected by such transitions. An anomalous temperature dependence of the DWF has indeed been reported from the ferroelectrics $BaTiO_3$ and $PbTiO_3$,[3] from the stoichiometric compounds $Ge_xSn_{1-x}Te$,[4] from the $A15$-structure compound Nb_3Sn,[5] etc.

Theoretical treatments concentrate upon the first term in the cumulant expansion of (1) anticipating that $\langle(\vec{Q}\cdot\vec{u})^2\rangle$ should dominate in an appropriate choice of the momentum transfer $\vec{Q}$ in the scattering process. Muzikář, Janovec, and Dvořák[6] as well as Bhide and Hedge[3] predicted a divergent mean-square sublattice displacement $\langle\vec{u}^2\rangle$ at T_c, using an Einstein-oscillator approximation for the soft optical-phonon mode,[7] whereas Schuster and Bostock[8] came to the same conclusion employing the traditional Debye model and relating the Debye temperature to the vanishing shear modulus $(C_{11} - C_{12})/2$ of Nb_3Sn at the transformation temperature. Finally, Rigamonti and Petrini[4] obtained a critical divergence, assuming an inappropriate dispersion curve for the soft optical-phonon branch. While these crude treatments are clearly inadequate, Borsa and Rigamonti[9] predicted a cusp-shaped anomaly of $\langle\vec{u}^2\rangle$ at T_c. This result was obtained assuming an Ornstein-Zernike expression for the Fourier transform $\langle\vec{u}(\kappa|\vec{q})\vec{u}(\kappa|-\vec{q})\rangle$ of the displacement correlation function which, therefore, has to be integrated over the Brillouin zone in order to obtain $\langle\vec{u}^2(\kappa\vec{l})\rangle$. As we shall see below, their quantitative predictions are not valid either.

We present in the following an investigation of the temperature dependence of the exponent of the DWF, quadratic in the momentum transfer, near structural phase transitions, not resting upon the harmonic approach, which is a high-frequency approximation. It will rather be shown that the mean-square sublattice displacements $\langle\vec{u}^2\rangle$ near critical points T_c are determined by the *renormalized static phonon frequencies*. Possible forms of soft phonon branches in the vicinity of T_c are analyzed from the point of view of lattice dynamics. Their implications on the behavior of the DWF at T_c and on the electron-paramagnetic-resonance (EPR) linewidth in the slow-motion regime—where the major part of the displacement fluctuations is slow in comparison with the magnetic relaxation they produce—are investigated. Critical exponents associated with a cusp-shaped anomaly of the DWF are estimated from scaling arguments and related

to those of the specific heat. The extent to which the anomaly of the DWF at T_c is related to the occurrence of a central peak and to which this anomaly might be detected experimentally is briefly discussed.

II. MICROSCOPIC FORMULATION

The quantity which we are interested in for our considerations concerning the DWF is the rigorous expression

$$\langle(\vec{Q}\cdot\vec{u})^2\rangle = \hbar\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}N^{-1}\sum_{\vec{q}}\vec{Q}\cdot\chi''_{\vec{u}\vec{u}}(\kappa\kappa|\vec{q},\omega)\cdot\vec{Q} \times\coth(\beta\hbar\omega/2)\,, \tag{2}$$

where the sum over wave vectors $\vec{q}$ is confined to the first Brillouin zone of the crystal of N unit cells. The fluctuation-dissipation theorem has been used in order to relate the equal-time displacement correlation function $\langle\vec{u}(\kappa\vec{l})\vec{u}(\kappa\vec{l})\rangle$ and the spectral function $\chi''_{\vec{u}\vec{u}}(\kappa\kappa|\vec{q},\omega)$ of the κth sublattice. This spectral function may be defined as the Fourier transform of the expectation value of the commutator of displacement operators at the inverse temperature $\beta=1/k_BT$.[10] For investigations in the vicinity of a structural phase transition it is useful to measure wave vectors $\vec{q}$ in the first Brillouin zone from the soft-mode wave vector $\vec{q}_0$ as origin [in ferroelectrics or in $A15$-structure compounds $\vec{q}_0=0$, of course; whereas in "antiferroelectrics" such as $SrTiO_3$, $\vec{q}_0=\vec{q}_R=(\pi/a)(1,1,1)$, for instance, where a is the lattice constant].

Since critical anomalies are attributed to long-range correlations we have to consider the contribution $\vec{q}\to 0$ at the transition temperature $T\to T_c$, and owing to the critical slowing down, we also have $\omega\to 0$.[11] Therefore, if critical divergences would exist, they were still obtained correctly by using $\coth(\beta\hbar\omega/2)\simeq 2k_BT_c/\hbar\omega$. As we shall show later, the mean-square displacement $\langle\vec{u}^2\rangle$ does only exhibit a cusp-shaped anomaly at T_c and no critical divergence. The critical exponents describing this cusp, however, are still obtained correctly from this approximation, since many studies have revealed[12] that "quantum effects" are irrelevant for the values of the exponents. Therefore, we deduce from Eq. (2) as $T\to T_c$,

$$\langle(\vec{Q}\cdot\vec{u})^2\rangle\simeq(k_BT_c/N)\sum_{\vec{q}}\vec{Q}\cdot\chi_{\vec{u}\vec{u}}(\kappa\kappa|\vec{q},0)\cdot\vec{Q}\,. \tag{3}$$

In a unit cell of s lattice particles the static displacement susceptibility

$$\chi_{\alpha\alpha'}(\kappa\kappa'|\vec{q},0)=\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\frac{\chi''_{\alpha\alpha'}(\kappa\kappa'|\vec{q}\omega)}{\omega} \tag{3a}$$

is an element of a $3s\times 3s$ matrix, since $\kappa=1,2,\ldots,s$ and the Cartesian components of the displacement operator $\vec{u}$ are denoted by $\alpha=1,2,3$.

A prominent feature of the present approach now is that the exponent of the DWF can still be reduced to the well-known formula

$$\langle(\vec{Q}\cdot\vec{u})^2\rangle=\frac{k_BT_c}{Nm_\kappa}\sum_{\vec{q},j}|\vec{Q}\cdot\vec{e}^{\,j}(\kappa\vec{q})|^2\frac{1}{\omega_j^2(\vec{q})} \tag{4}$$

in diagonalizing the $3s\times 3s$ matrix $\underline{\chi}(\vec{q},0)$ by means of the eigenvalue equation of its inverse,

$$\sum_{\alpha'\kappa'}(m_\kappa m_{\kappa'})^{-1/2}\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q},0)\,e^j_{\alpha'}(\kappa'\vec{q}) =\omega_j^2(\vec{q})\,e^j_\alpha(\kappa\vec{q})\,, \tag{5}$$

where m_κ and $m_{\kappa'}$ denote lattice-particle masses. The eigenvalues of $\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}0)$ for each value of $\vec{q}$ thus are the $3s$ squares of the *renormalized static phonon frequencies*, $\omega_j^2(\vec{q})$, with the eigenvectors $e^j_\alpha(\kappa\vec{q})$. One should keep in mind, however, that these $\omega_j^2(\vec{q})$ may considerably deviate from the harmonic phonon frequencies. Nevertheless, Eq. (4) is valid irrespective of the complicated structure of the frequency dependence of the displacement correlation function near T_c, being reflected, for instance, by the dispersion relation given in Ref. 10:

$$\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}z)=-m_\kappa\left(z^2\delta^{\kappa\kappa'}_{\alpha\alpha'}-\frac{\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}0)}{m_\kappa} +z\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\frac{\gamma_{\alpha\alpha'}(\kappa\kappa'|\vec{q}\omega)}{\omega(\omega-z)}\right), \tag{6}$$

where $\gamma_{\alpha\alpha'}(\kappa\kappa'|\vec{q}\omega)$ is a generalized frequency-dependent phonon damping function. While a full microscopic understanding of this quantity near displacive phase transitions is still lacking,[13] it is well known[10] that its minus first frequency moment connects the inverse of the low- and high-frequency displacement response:

$$\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q},\infty)-\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q},0) =m_\kappa\int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\frac{\gamma_{\alpha\alpha'}(\kappa\kappa'|\vec{q}\omega)}{\omega}\,. \tag{6a}$$

The normal modes of the crystal in the harmonic approximation are then approximate eigenvalues of the inverse of the high-frequency response function $\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q},\infty)$ of (6a), to be denoted by

$$\omega_j^2(\vec{q},\infty)=\omega_j^2(\vec{q})+\delta_j^2(\vec{q})\,. \tag{6b}$$

These frequencies $\omega_j^2(\vec{q},\infty)$, which may readily be calculated microscopically,[14] therefore, will differ from the renormalized static phonon frequencies $\omega_j^2(\vec{q})$ entering into Eq. (4) of the DWF exponent by the amount $\delta_j^2(\vec{q})$, to be obtained from

$$\int_{-\infty}^{+\infty}d\omega\,\gamma_{\alpha\alpha'}(\kappa\kappa'|\vec{q},\omega)/\pi\omega\,.$$

A microscopic determination of the $\omega_j^2(\vec{q})$, in general, turns out to be considerably more compli-

cated. A possible program of such a calculation may start from a rigorous functional-derivative expression of the wave-vector- and frequency-dependent phonon self-energy, [15]

$$M_{\alpha_1\alpha_2}(\kappa_1\kappa_2|\vec{q}z) = \int_0^{-i\beta} d(t_1 - t_2)\, e^{iz(t_1 - t_2)}\, N^{-1} \times \sum_{\vec{l}_1\vec{l}_2} e^{-i\vec{q}\cdot\vec{R}(\lambda_1\lambda_2)} (m_{\kappa_1} m_{\kappa_2})^{-1/2} \frac{\delta}{\delta\langle X_{\alpha_2}(2)\rangle} \left\langle \frac{\partial H}{\partial X_{\alpha_1}(1)} \right\rangle, \tag{7}$$

of the Hamiltonian H of the crystal with lattice-particle position operators $X_{\alpha_1}(1)$ and $X_{\alpha_2}(2)$. The $t_1 - t_2$ integration in (7) is along the imaginary time-temperature axis in the interval $(0, -i\beta)$, $\vec{R}(\lambda_1\lambda_2) \equiv \langle\vec{X}(\lambda_1)\rangle - \langle\vec{X}(\lambda_2)\rangle$, and $1 \equiv \lambda_1 t_1$, where $\lambda_1 \equiv \kappa_1 \vec{l}_1$. Since the phonon self-energy is connected with the inverse of the displacement correlation function via the Dyson equation[15]

$$\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}z) = -m_\kappa [z^2 \delta^{\kappa\kappa'}_{\alpha\alpha'} - M_{\alpha\alpha'}(\kappa\kappa'|\vec{q}z)], \tag{6c}$$

its static value

$$\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}, 0) = m_\kappa M_{\alpha\alpha'}(\kappa\kappa'|\vec{q}, 0) \tag{6d}$$

is determined by the static ($z \to 0$) phonon self-energy. Equations (7) and (6d) are rigorous but formal. The utility of the approach is that consistent approximations can be generated for $M_{\alpha\alpha'}(\kappa\kappa'|\vec{q}, 0)$ and $\chi^{-1}_{\alpha\alpha'}(\kappa\kappa'|\vec{q}, 0)$, respectively, using the functional-derivative technique. [15] A detailed development of such consistent approximations, though feasible, is extensive to carry out, in particular with regard to a determination of temperature anomalies including effects of fluctuations, which is not our present concern.

The important point in this context is, however, that these frequencies $\omega^2_j(\vec{q})$ and *not the zeros* of the inverse of the response function of Eq. (6), which would be the physically observable phonon "peaks," have to be inserted in Eq. (4) for the exponent of the DWF. These features of our theory might well be elucidated in terms of the well-known Maxwell-Drude or Debye interpolation formula[16]

$$\chi^{-1}_{j_0}(\vec{q}, z) = -m\left[z^2 - \omega^2_{j_0}(\vec{q}) + iz\left(\Gamma_{j_0} + \frac{\tau_{j_0}\delta^2_{j_0}}{1 - i\tau_{j_0}z}\right)\right], \tag{8}$$

which has frequently been used[17] in order to analyze experimental data of those branches j_0 of the "diagonalized" form of (6) which exhibit a soft-mode behavior. The zeros of (8) allow for the experimentally observed three-peak structure: a central peak at $\omega = 0$ in addition to two "phonon" peaks, approximately located at $\omega \simeq \pm[\omega^2_{j_0}(\vec{q}) + \delta^2_{j_0}(\vec{q})]^{1/2}$, provided that $\omega\tau_{j_0} \gg 1$ and that Γ_{j_0} is sufficiently small.

From our discussion it is clear that the central-peak parameters $\delta^2_{j_0}$ and τ_{j_0} do not enter directly into the squares of the static frequencies $\omega^2_{j_0}(\vec{q})$ which, in turn, enter into the DWF at T_c through Eq. (4). Anomalous behavior of the DWF at T_c in our approach, therefore, must result from a critical behavior of some specific phonon branches $\omega^2_j(\vec{q})$. A derivation of meaningful expressions for the temperature variation of such phonon branches in accord with our microscopic formulation and possible implications for the DWF exponent at T_c will be presented in Sec. III.

III. LATTICE DYNAMICS AND EXPLICIT MODEL CALCULATIONS

In order to estimate the temperature anomaly in the DWF on the basis of the microscopic approach outlined above one needs suitable analytical forms of the dispersion surfaces of those renormalized static phonon branches $\omega^2_{j_0}(\vec{q})$ which become soft near a particular wave vector $\vec{q}_0$. In practice this may be achieved with the aid of a small $\vec{q}$ expansion around $\vec{q}_0$. First, the regular part of the inverse of the static displacement susceptibility (6d)—modified via multiplication by a factor $e^{-i\vec{q}\cdot[\vec{r}(\kappa) - \vec{r}(\kappa')]}$, where $\vec{r}(\kappa)$ denotes lattice-particle positions in the unit cell—is expanded around $\vec{q}_0$ and combined with possible long-range-part contributions to give

$$m^{-1}_\kappa \chi^{-1}_{\rho\rho'}(\vec{q} - \vec{q}_0, 0) = M^{(0)}_{\rho\rho'}(\vec{q}_0) + iq_\beta M^{(1)}_{\rho\rho',\beta}(\vec{q}_0) + q_\beta q_{\beta'} M^{(1)}_{\rho\rho',\beta\beta'}(\vec{q}_0) + \cdots . \tag{9}$$

We have used the abbreviations ρ for a pair of subscripts (α, κ) and $\beta = 1, 2, 3$.

In further developing the program we shall particularly be concerned with three specific types of structural phase transitions[17]: (a) phase transitions occurring, e.g., in the "antiferroelectric" $SrTiO_3$ which result from an instability of the crystal against a threefold-degenerate optical R_{25} mode at the zone corner; (b) phase transitions occurring, e.g., in the $A15$ compound Nb_3Sn which arise from an instability of the crystal against a transverse-acoustic mode with wave vector $\vec{q}$ along [110] and polarization vector $\vec{e}$ along $[1\bar{1}0]$; (c) phase transitions occurring, e.g., in uniaxial ferroelectrics, such as triglycine sulfate (TGS) or RbH_2PO_4, where long-range forces of dipolar nature give rise to modifications.

In the examples of $SrTiO_3$ and Nb_3Sn mentioned above, three low-energy eigenstates of the $3s \times 3s$ matrix $\chi^{-1}_{\rho\rho'}(\vec{q}_0, 0)$ of interest in the vicinity of the phase transition are threefold degenerate at $T > T_c$. In $SrTiO_3$ these three states describe rotations of oxygen octahedra about the j_0th cubic axis, and the common eigenvalue $\omega^2_{j_0}(\vec{q}_R) \equiv \omega^2_0$ ($j_0 = 1, 2, 3$) denotes the threefold degenerate optical soft mode at the R point. In Nb_3Sn the three states describe uniform displacements of the entire crystal with the long-

wavelength ($\vec{q}_0 \to 0$) acoustic phonons $\omega^2_{j_0}(0) = \omega_0^2 \equiv 0$ ($j_0 = 1, 2, 3$). The corresponding eigenstates may be designated in both cases as: $e^1(\rho\vec{q}_0)$, $e^2(\rho\vec{q}_0)$, $e^3(\rho\vec{q}_0)$.

In order to obtain the required dispersion curves $\omega^2_{j_0}(\vec{q})$ we form a truncated 3×3 matrix $\hat{\chi}^{-1}_{\beta\beta'}(\vec{q} - \vec{q}_0, 0)$, which by construction at $\vec{q} = \vec{q}_0$ has the eigenvalues $\omega^2_{j_0}(\vec{q}_0) \equiv \omega_0^2$ ($j_0 = 1, 2, 3$) described above. One may obtain $\hat{\chi}^{-1}_{\beta\beta'}$ from $\chi^{-1}_{\rho\rho'}$ of (9) by the transformation

$$\hat{\chi}^{-1}_{\beta\beta'}(\vec{q} - \vec{q}_0, 0) = w^T_\beta(\rho\vec{q}_0)\chi^{-1}_{\rho\rho'}(\vec{q} - \vec{q}_0, 0)w_{\rho'}(\beta'\vec{q}_0) \qquad (9a)$$

(notice the summation convention for repeated subscripts ρ and ρ'), where the $3\times3s$ matrix

$$\{w_\beta(\rho\vec{q}_0)\} = m_\rho^{-1}\{e^1(\rho\vec{q}_0),\ e^2(\rho\vec{q}_0),\ e^3(\rho\vec{q}_0)\}\ . \qquad (9b)$$

For *cubic symmetry* we find the required result:

$$\hat{\chi}^{-1}_{\beta\beta'}(\vec{q}, 0) = [\omega_0^2 + \lambda_2\vec{q}^2 + (\lambda_1 - \lambda_2)q_\beta^2] \times \delta_{\beta\beta'} + \lambda_3 q_\beta q_{\beta'}(1 - \delta_{\beta\beta'}), \qquad (10)$$

where the parameters ω_0^2, λ_1, λ_2, and λ_3 may be expressed in terms of the microscopic expansion coefficients $M^{(0)}$, $M^{(1)}$, $M^{(2)}$ of (9). On the other hand, the parameters λ_1, λ_2, and λ_3 may be related to the staggered isothermal elastic constants in the case of $SrTiO_3$, where $\omega_0^2 \neq 0$, and to the isothermal elastic constants in the case of Nb_3Sn, where $\omega_0^2 \equiv 0$. One finds

$$\lambda_1 = C_{11}, \quad \lambda_2 = C_{44}, \quad \lambda_3 = C_{12} + C_{44}\ .$$

The derivation of Eq. (10) indicated above, therefore, represents an extension of the method of long waves of Born and Huang[18] in two respects: First it does not rest upon the harmonic approximation and is related to the *general compressibility sum rule*[15,19]; second, it is not restricted to the $\vec{q}_0 = 0$ center of the Brillouin zone. The confinement to cubic symmetry of the final formula (10) has been chosen for simplicity only.

The dispersion surfaces of the soft renormalized static phonon branches near a particular wave vector $\vec{q}_0$ for sufficiently small $\vec{q}$, finally, are eigenvalues of the 3×3 matrix $\hat{\chi}^{-1}_{\beta\beta'}(\vec{q} - \vec{q}_0, 0)$ of (10). The coefficients ω_0^2, λ_1, λ_2, λ_3 entering into these eigenvalues, instead of being computed microscopically from $M^{(0)}$, $M^{(1)}$, and $M^{(2)}$, here are treated as follows: (i) The temperature dependence of that term in $\omega^2_{j_0}(\vec{q})$ being responsible for the instability in the limit $\vec{q} \to 0$ is taken from the static scaling behavior of the inverse of the critical susceptibility $\lim_{\vec{q}\to0}\chi^{-1}_{j_0}(\vec{q}) \propto |1 - T/T_c|^\gamma$. (ii) The temperature dependence of all the other terms is much weaker. It can be estimated from static scaling relations[12] for the wave-vector-dependent susceptibility,

$$\chi^{-1}_{j_0}(\vec{q}) = |1 - T/T_c|^\gamma f_{j_0}(\xi q) = |1 - T/T_c|^\gamma [f^{(0)}_{j_0} + f^{(1)}_{j_0}(\xi^2 q^2) + \cdots],$$

where $\xi = \xi_0|1 - T/T_c|^{-\nu}$ is the correlation length of the fluctuations, which yields for the temperature dependence of the second term $|1 - T/T_c|^{\gamma-2\nu} = |1 - T/T_c|^{-\eta\nu}$. Note that the exponent η is very small in three dimensions.[12]

The analytical expressions of the $\omega^2_{j_0}(\vec{q})$ to be obtained from (10) are needed for the $\vec{q}$ integration over the Brillouin zone in Eq. (4). They are particularly simple along the main symmetry directions of the crystal. Simple analytical expressions for arbitrary directions may be obtained, however, by adequate approximations for the three specific systems:

(a) For the threefold degenerate R-corner optical mode in $SrTiO_3$, we obtain ($j_0 = 1, 2, 3$)

$$\omega^2_{j_0}(\vec{q}) \simeq \hat{\omega}_0^2[|1 - T/T_c|^\gamma + \vec{q}^2/K^2 - (1 - \Delta)q^2_{j_0}/K^2 + \cdots], \quad \vec{q} \to 0 \qquad (10a)$$

in neglecting the off-diagonal elements of (10).[20] Hence the anisotropy parameter $\Delta \equiv \lambda_1/\lambda_2$, while the critical amplitude and critical exponent of the susceptibility are denoted by $\hat{\omega}_0^2$ and γ, respectively, whereas $\hat{\omega}_0^2/K^2 \equiv \lambda_2$.

(b) For the acoustic mode in Nb_3Sn which becomes soft provided it is polarized along $[1\bar{1}0]$ with wave vector $\vec{q} \parallel [110]$, we obtain

$$\omega^2_{T_1}(\vec{q}) \simeq u_0^2 q^2[|1 - T/T_c|^\gamma + (1 - \Delta)q_\perp^2/q^2 + q^2/K^2 + \cdots], \quad \vec{q} \to 0 \qquad (10b)$$

if the two off-diagonal elements of (10), vanishing rigorously for polarization and direction for which softening occurs, are neglected; then $q_\perp$ is the component of $\vec{q}$ perpendicular to the "soft" direction, and $u_0^2|1 - T/T_c|^\gamma = (\lambda_1 + \lambda_2 - \lambda_3)/2$ denotes the drastically softened shear modulus as $T \to T_c$, if the abbreviation

$$u_0^2(1 - \Delta) \equiv \lambda_3^2[1 - 4(\lambda_1 - \lambda_2)^2/\lambda_3]/2$$

is used. The additional term $u_0^2q^4/K^4$ in (10b) goes beyond Eq. (10); however, terms of order $\vec{q}^4$ have to be added in order to guarantee an increase of $\omega^2_{T_1}(\vec{q})$ for increasing $|\vec{q}|$ along [110].

(c) For modifications of (a) due to long-range forces of dipolar nature, if j_0 is the incipient ferroelectric axis,[21,22]

$$\omega^2_{j_0}(\vec{q}) \simeq \hat{\omega}_0^2[|1 - T/T_c|^\gamma + \vec{q}^2/K^2 - (1 - \Delta)q^2_{j_0}/K^2 + \lambda q^2_{j_0}/q^2 + \cdots], \quad \vec{q} \to 0\ . \qquad (10c)$$

Equations (10a)–(10c) represent valid analytical forms in the "hydrodynamic" regime,[11] $q\xi \ll 1$, only. If we were disregarding this fact, we could evaluate Eq. (4) using (10a)–(10c) to obtain the critical contributions to $\langle\vec{u}^2\rangle$ for cubic symmetry, where it reduces to

$$\langle(\vec{Q}\cdot\vec{u})^2\rangle = \tfrac{1}{3}\vec{Q}^2\cdot\langle\vec{u}^2\rangle\ . \qquad (4a)$$

Therefore, in the case of the soft optical R_{25} corner mode,[23]

$$\langle \vec{u}^2 \rangle_{cr} = \text{const} - \frac{k_B T_c}{m_\kappa} \frac{v}{4\pi^2} \frac{K^3}{\hat{\omega}_0^2 (1-\Delta)^{1/2}} \times \ln \left| \frac{1+(1-\Delta)^{1/2}}{1-(1-\Delta)^{1/2}} \right| |1 - T/T_c|^{\gamma/2}, \quad T \to T_c \tag{11a}$$

while in the case of the soft transverse acoustic mode,

$$\langle \vec{u}^2 \rangle_{cr} = \text{const} - \frac{k_B T_c}{m_\kappa} \frac{v}{4\pi} \frac{K}{u_0^2 (1-\Delta)} |1 - T/T_c|^{\gamma/2}, \quad T \to T_c \tag{11b}$$

and in the case of long-range forces in ferroelectrics, neglecting, for simplicity, the anisotropy term $1-\Delta \to 0$ in (10c) and using $\gamma = 1$,

$$\langle \vec{u}^2 \rangle_{cr} = \text{const} - \frac{k_B T_c}{m_\kappa} \frac{v}{16\pi} \frac{K^3}{\hat{\omega}_0^2 \sqrt{\lambda}} \times |1 - T/T_c| \ln(4K^2 |1 - T/T_c|), \quad T \to T_c . \tag{11c}$$

Here, $v \equiv V/N$ denotes the volume of the unit cell. Equation (11a) compares with Ref. 9 except for the fact that there anisotropy has not been accounted for explicitly.

In deriving Eqs. (11a)–(11c), the integrals over the Brillouin zone have been carried out using a spherical cutoff. Therefore, the leading constant term could not be obtained reliably. Yet, more important, both the critical exponents and the prefactors are not reliable either, since Eqs. (10a)–(10c) valid for $q\xi \ll 1$ have also been used for $q\xi > 1$, i.e., outside their range of validity. In Sec. V we shall point out that this fact may lead to a weaker singularity of the DWF than the one predicted by Eqs. (11a)–(11c).

IV. EPR LINEWIDTH OF SLOW-MOTION REGIME

Local time-dependent displacement fluctuations $\langle \vec{u}(\kappa \vec{1} t) u(\kappa \vec{1} 0) \rangle$ of systems undergoing structural phase transitions may also be investigated by electron-paramagnetic-resonance (EPR) linewidth measurements.[24] At certain paramagnetic impurity centers (e.g., Fe^{3+}-V_0 pair centers in $SrTiO_3$) such time-dependent displacement fluctuations contribute to the EPR linewidth ΔH due to an effective magnetic field generated by local displacements. Provided we have a linear relationship between the resonance magnetic field at time t and the local displacements $\vec{u}(\kappa \vec{1} t)$, the contribution to the EPR linewidth may be approximated[24,25] by

$$(\Delta H)^2 \propto \int_{-\omega_1}^{+\omega_1} d\omega \left(\int_{-\infty}^{+\infty} dt \langle u_\alpha(\kappa \vec{1} t) u_\alpha(\kappa \vec{1} 0) \rangle e^{i\omega t} \right), \tag{12}$$

where the cutoff frequency ω_1 is equivalent to the linewidth ΔH. Using the fluctuation-dissipation theorem in the vicinity of T_c as discussed in Sec. II we may write

$$\int_{-\infty}^{+\infty} dt \langle u_\alpha(\kappa \vec{1} t) u_\alpha(\kappa \vec{1} 0) \rangle e^{i\omega t} \propto \frac{k_B T_c}{\pi \omega} \sum_{\vec{q}} \chi''_{\alpha\alpha}(\kappa\kappa | \vec{q}, \omega), \tag{13}$$

and therefore

$$(\Delta H)^2 \propto k_B T_c \sum_{\vec{q}} \int_{-\omega_1}^{+\omega_1} \frac{d\omega}{\pi} \frac{\chi''_{\alpha\alpha}(\kappa\kappa | \vec{q}, \omega)}{\omega} . \tag{14}$$

In the *"slow-motion" regime*, the fluctuations are assumed to be concentrated at frequencies low in comparison with the magnetic relaxation they produce. Thus the integration in (14) is extended to infinity and using (3a) we obtain

$$(\Delta H)_s^2 \propto k_B T_c \sum_{\vec{q}} \chi_{\alpha\alpha}(\kappa\kappa | \vec{q}, 0) , \tag{15}$$

which according to Eq. (3) implies that $(\Delta H)_s^2$ is proportional to the instantaneous local displacement fluctuations $\langle \vec{u}^2 \rangle$. The integration over the Brillouin zone in (15) can then be carried out along the lines discussed above.

In fact, using a phonon dispersion $\omega_{j_0}^2(\vec{q})$ equivalent to (10a) the integral leading to Eq. (11a) has been evaluated in Refs. 24 and 26. The result of these authors is different from Eq. (11a), however, since they approximated the Brillouin zone by an ellipsoid with one axis proportional to $1/\sqrt{\Delta}$, which is inadequate for $\Delta \ll 1$, giving rise to a spurious $\Delta^{-1/2}$ singularity for $\Delta \to 0$.

Of course, the discussion of the EPR linewidth outlined in Eq. (12)–(15) is somewhat qualitative and a more refined treatment seems necessary.[27] However, in the framework of the validity of Eq. (15) the temperature dependence of the EPR linewidth in the slow-motion regime is the same as that of the exponent of the DWF and can also be obtained from the scaling analysis of Sec. V.

V. PHENOMENOLOGICAL SCALING THEORY

The predictions on the temperature dependence of the DWF exponent and of the EPR linewidth in the vicinity of T_c obtained in Secs. III and IV still suffer from the fact that in the course of their derivation approximate forms of soft-phonon dispersion curves have been used outside the range of their "hydrodynamic" validity.

In this section we want to indicate how phenomenological scaling theory might be applied in order to find that the cusp-shaped anomalies to be observed actually should even be weaker than those predicted above. This result is in accord with renormalization-group arguments implying[28] that the critical behavior of the local-order-parameter susceptibility $\langle \mu^2 \rangle$ should be that of the internal energy or even weaker.[29] These arguments can be ex-

ploited more explicitly for structural phase transitions by specifying the local order parameter

$$M \equiv \langle \mu^{j_0}(\vec{q}_0) \rangle \propto (1 - T/T_c)^{\beta}, \quad T \to T_c \tag{16}$$

with order-parameter exponent β. Since $M = \langle \mu^{j_0}(\vec{q}_0) \rangle$ should denote that *static displacement* of the particular normal mode of the high-temperature phase (branch j_0 and wave vector $\vec{q}_0$) which represents the distortion of the low-temperature phase, the wave-vector-dependent order-parameter operator $\mu^{j_0}(\vec{q})$ is connected with the operators $u(\kappa\vec{l})$ of the displacements of the κth lattice particle in the $\vec{l}$th unit cell from lattice sites $R(\kappa\vec{l})$ according to

$$\mu^{j_0}(\vec{q}) = N^{-1/2} \sum_{\kappa\vec{l}} (\sqrt{m_\kappa})\, \vec{e}^{\,j_0}(\kappa | -\vec{q}) \cdot \vec{u}(\kappa\vec{l})\, e^{-i\vec{q}\cdot\vec{R}(\kappa\vec{l})} . \tag{17}$$

One then may introduce a local "space-dependent" order-parameter operator of the $\vec{l}$th unit cell[30]:

$$\mu^{j_0}(\vec{l}) = N^{-1/2} \sum_{\vec{q}} \mu^{j_0}(\vec{q})\, e^{i\vec{q}\cdot\vec{R}(\vec{l})} , \tag{17a}$$

with the required static part

$$\langle \mu^{j_0}(\vec{l}) \rangle = M e^{i\vec{q}_0\cdot\vec{R}(\vec{l})} . \tag{17b}$$

Hence, the critical behavior of the mean-square displacements, being written as

$$\langle \vec{u}^2(\kappa\vec{l}) \rangle = \frac{k_B T_c}{N m_\kappa} \sum_{\vec{q},j} |\vec{e}^{\,j}(\kappa\vec{q})|^2 [\chi^j_{\mu\mu}(\vec{q}, 0) - M^2 \delta_{jj_0} \delta(\vec{q} - \vec{q}_0)] , \tag{17c}$$

arises from the contribution $\chi^j_{\mu\mu}(\vec{q}_0, 0) - M^2$, and implying the renormalization-group arguments stated above, one immediately predicts

$$\begin{aligned} \langle \vec{u}^2 \rangle_{cr} &\propto C_0 - C_1^+ \epsilon^{1-\alpha} && \text{for } T > T_c, \ \epsilon \to 0 , \\ \langle \vec{u}^2 \rangle_{cr} &\propto C_0 - C_1^- \epsilon^{1-\alpha} - C_2^+ \epsilon^{2\beta} && \text{for } T \lesssim T_c, \ \epsilon \to 0 , \end{aligned} \tag{18}$$

where $\epsilon = |1 - T/T_c|$.

On the other hand, Eq. (11a) predicts a critical behavior $\langle \vec{u}^2 \rangle_{cr} \propto K^3 \epsilon^{\gamma/2} \propto \epsilon^{\nu(1+\eta)}$ is static scaling is used in order to estimate the critical temperature dependence of K as indicated in Sec. III. Using scaling laws $d\nu = 2 - \alpha = \gamma + 2\beta$ and $\gamma = \nu(2 - \eta)$, for dimensionality $d = 3$,[31] we infer $\nu(1 + \eta) = 2\beta$; i. e., the critical behavior predicted by (11a) agrees with that stated in (18) below T_c only, whereas the singularity predicted by (18) above T_c is $\epsilon^{1-\alpha}$ and therefore weaker (usually $\beta \simeq 0.30$–0.37 while the specific-heat exponent[12] $\alpha \approx 0.0$–0.1).

In the remainder of this section we shall now indicate the calculation of $\sum_q \langle \mu^{j_0}(\vec{q}) \mu^{j_0}(-\vec{q}) \rangle$ by means of static scaling similar to the approach of Sec. III for calculating $\sum_q \omega_j^{-2}(\vec{q})$. In contrast to the integration over the inverse of the renormalized static phonon frequencies $\omega_j^{-2}(\vec{q})$ before, the anisotropy in the integration over $\langle \mu^{j_0}(\vec{q}) \mu^{j_0}(-\vec{q}) \rangle$ now does not play a crucial role and will be disregarded therefore. The important feature is, however, that the temperature derivative of $\langle \mu^{j_0}(\vec{l})^2 \rangle - M^2$ might be related to the critical part of the specific heat which allows us to prevent the problems with the cutoff dependence in determining $\langle \vec{u}^2 \rangle_{cr}$, at least as far as the critical exponents are concerned.

We thus start from the scaling expression

$$\chi^j_{\mu\mu}(\vec{q}, 0) = M^2 \delta_{jj_0} \delta(\hat{\vec{q}}) + \hat{q}^{-2+\eta} F_0^{\pm}(\epsilon^\nu/\hat{q}) + \hat{q}^{y_1} F_1^{\pm}(\epsilon^\nu/\hat{q}) + \cdots \tag{19}$$

for $|\hat{q}| = |\vec{q} - \vec{q}_0| \to 0$, $T \to T_c$, yet arbitrary values of $\epsilon^\nu/\hat{q}$. The $\pm$ signs refer to above and below T_c, respectively. The second term on the right-hand side of (19) is the usual scaling expression, while the third and further terms are corrections to scaling. Therefore, the exponents must satisfy $-2 + \eta < y_1 < \cdots$.

Consistent with our previous findings it follows from (19) that

$$\langle \mu^{j_0}(\vec{l})^2 \rangle - M^2 = \sum_{\hat{\vec{q}}} \hat{q}^{-2+\eta} F_0^{\pm}(0) + \cdots$$

as $T \to T_c$ and hence approaches a constant. Again this constant cannot be obtained reliably, since the main contribution comes from a cutoff $q \simeq q_c$, where Eq. (19) is no longer a valid expression. In order to obtain the temperature dependence resulting from (19) we consider the following derivative:

$$\begin{aligned} \frac{\partial}{\partial\epsilon} [\langle \mu^{j_0}(\vec{l})^2 \rangle - M^2] &= \nu \epsilon^{\nu-1} \sum_{\hat{\vec{q}}} [\hat{q}^{-3+\eta} F_0'^{\pm}(\epsilon^\nu/\hat{q}) + \hat{q}^{y_1-1} F_1'^{\pm}(\epsilon^\nu/\hat{q}) + \cdots] \\ &\propto \nu \epsilon^{\nu(1+\eta)-1} \left(\int_0^{\hat{q}_c/\epsilon^\nu} dx\, x^{\eta-1} F_0'^{\pm}(x^{-1}) + \epsilon^{\nu(2+y_1-\eta)} \int_0^{\hat{q}_c/\epsilon^\nu} dx\, x^{1+y_1} F_1'^{\pm}(x^{-1}) + \cdots \right) , \end{aligned} \tag{20}$$

where $F'(y) = \partial F(y)/\partial y$. If the main contribution to the integral $\int dx\, x^{\eta-1} F_0'^{\pm}(1/x)$ came from $x \simeq 1$, we could replace the upper limit by infinity and would obtain a temperature dependence $\epsilon^{\nu(1+\eta)}$ for the critical contribution of $\langle \vec{u}^2 \rangle$, *provided* this contribution were not canceled by one of the corrections. Such a cancellation may indeed occur, however, since in Eq. (20) we are considering a correction

to the leading scaling contribution only, giving a constant. *If* the main contribution to this integral came from $x \gg 1$, *or if* such a cancellation took place, a weaker singularity of $\langle \vec{u}^2 \rangle_{cr}$ would be obtained. In order to estimate the exponent of the singularity, we relate the critical part of $\langle \vec{u}^2 \rangle$ to the critical part of the interaction energy, following a method of Griffiths.[32] One may start from a model Hamiltonian which contains bilinear interaction of the local order parameter $\mu^{j_0}(\vec{l})$ in different cells, only:

$$\mathcal{H} \propto \sum_{\vec{l}\vec{l}'} \varphi(\vec{l}\vec{l}')\mu^{j_0}(\vec{l})\mu^{j_0}(\vec{l}') + \sum_{\vec{l}} f(\mu^{j_0}(\vec{l})) \,. \qquad (21)$$

Since a structural transition then can be induced by an indefinite matrix $\varphi(\vec{l}\vec{l}')$ with the over-all stability being ensured by a positive quartic anharmonicity ($b > 0$) in the "single-ion terms" $f(\mu^{j_0}(\vec{l})) = a\mu^{j_0}(\vec{l})^2 + b\mu^{j_0}(\vec{l})^4$, such and similar models have widely been used for ferroelectrics[22] and other structural phase transitions. Starting from the general Hamiltonian of lattice dynamics in the adiabatic approximation,

$$H = \tfrac{1}{2}\dot{u}_\alpha(\lambda) m_\lambda \dot{u}_\alpha(\lambda) + \sum_{n=0}^{\infty} \frac{1}{n!} V_{\alpha_1 \cdots \alpha_n}(\lambda_1 \cdots \lambda_n) u_{\alpha_1}(\lambda_1) \cdots u_{\alpha_n}(\lambda_n) \,,$$

one may attempt to justify such models by first introducing local order parameters as defined in (17a), and second, invoking renormalization-group arguments[33] in order to infer that higher-order correlated terms $[\mu^{j_0}(\vec{l})\mu^{j_0}(\vec{l}')\mu^{j_0}(\vec{l}'')$, etc.] should yield irrelevant corrections to the critical behavior, only, apart from multicritical points.[34] Renormalization-group arguments may further be used in order to anticipate a critical part of the internal energy of the form

$$\langle \mathcal{H} \rangle_{cr} = \sum_{\vec{q}} \varphi^{eff}(\vec{q}) \langle \mu^{j_0}(\vec{q})\mu^{j_0}(q) \rangle \,, \qquad (22)$$

where $\varphi^{eff}(\vec{q})$ is the Fourier transform of the effective order-parameter interaction, nonsingular at T_c. The critical part of the specific heat then is obtained from $C_{cr} \propto \partial \langle \mathcal{H} \rangle_{cr} / \partial \epsilon$ by expanding $\varphi^{eff}(\vec{q})$ in powers of $\hat{q}$:

$$C_{cr} \propto \varphi_0^{eff} \left(\frac{\partial M^2}{\partial \epsilon} + \epsilon^{\nu(1+\eta)-1} \int_0^{\hat{q}_c'/\epsilon^\nu} dx\, x^{\eta-1} F_0'^{\pm}(x^{-1}) + \epsilon^{\nu(3+y_1)-1} \int_0^{\hat{q}_c'/\epsilon^\nu} dx\, x^{1+y_1} F_1'^{\pm}(x^{-1}) \right)$$
$$+ \tfrac{1}{2}[\nabla_q \varphi^{eff}(\hat{\vec{q}})]^2|_{\hat{q}=0} \epsilon^{\nu(3+\eta)-1} \int_0^{\hat{q}_c'/\epsilon^\nu} dx\, x^{1+\eta} F_0'^{\pm}(x^{-1}) \cdots \,, \qquad (22a)$$

where $\hat{q}_c'$ is a cutoff whose order of magnitude is given by the inverse range of the interaction. Above T_c we have $\partial M^2/\partial \epsilon = 0$ and since $C_{cr} \propto \epsilon^{-\alpha}$, it then follows that no contributions proportional to $\epsilon^{\nu(1+\eta)-1}$ may occur. Since the coefficient of φ_0^{eff} is equivalent to $\partial \langle \mu^2(\vec{l}) \rangle / \partial \epsilon$ in Eq. (20), it follows that the singularity of $\partial \langle \mu^2(\vec{l}) \rangle / \partial \epsilon$ is at most $\epsilon^{-\alpha}$. It may even be weaker, since there may be further contributions proportional to $\epsilon^{-\alpha}$ in Eqs. (22a) which are absent in Eq. (20), consistent with the behavior of the Ising mode.[29] In the general case Eq. (18) will hold, but the amplitudes $C_1^{\pm}$ cannot be related to the amplitude factor of the singular part of the internal energy.

VI. CONCLUSIONS

Our concern in this paper was to consider the Debye-Waller factor at structural phase transitions. From a lattice-dynamical point of view it has been pointed out that $\langle \vec{u}^2 \rangle$ remains finite at all these transitions and that $\langle \vec{u}^2 \rangle$ is unaffected by the existence of a central peak. Thus, it has been found that the DWF has a cusp at T_c, the leading singularity being described by $\epsilon^{\nu(1+\eta)} = \epsilon^{2\beta}$ below T_c and by $\epsilon^{1-\alpha}$ above T_c, respectively (note that logarithmic factors, as occurring in ferroelectrics,[22] may be represented by choosing $\alpha = 0$). The relevance of these results for EPR linewidth measurements has been pointed out. A prediction for the associated prefactors is hard to obtain: it can only be said that the ratio of the critical amplitude of the DWF and its regular part should have the same order of magnitude as the ratio of the critical amplitude of the internal energy and its regular part. Therefore, the observability of this cusp in neutron scattering, x-ray scattering, or Mössbauer-fraction experiments may be questionable in unfavorable cases, where the amplitudes of the specific-heat singularity are small, e.g., $SrTiO_3$. In addition, owing to experimental reasons the singularity in the DWF may be obscured by other critical effects like critical scattering etc.

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