Dislocations and structural phase transitions involving an increase in the elementary cell

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The effects of dislocations are studied for crystals in which a structural phase transition is accompanied by an increase in the volume of the elementary cell. The equilibrium distribution of the order parameter is calculated for systems with and without continuous degeneracy. In the absence of continuous degeneracy, a dislocation domain wall structure is formed. The influence of the wall structure on the thermodynamic anomalies, light scattering, and attenuation of sound and the soft mode is studied.

1. INTRODUCTION

Many phase transitions are accompanied by an increase in the volume of the elementary cell (see, e.g., Ref. 1). Because such transitions reduce the translational symmetry and not all of the dislocations in the low-symmetry phase remain filled, the resulting strong topological interaction between the dislocations and the order parameter η distorts the equilibrium distribution of the latter. The nature of the distortion depends on the symmetry of the order parameter. If η is symmetric under a continuous group of transformations (as is the case, e.g., for an incommensurate charge density wave), a vortex in η is associated with each dislocation. In the absence of such symmetry, a domain wall is associated with the dislocation. In the latter case if the crystal contains a forest of parallel dislocations, a domain wall structure forms in which each wall extends between two dislocations. Such a structure has been observed in gadolinium molybdate, for example.[2]

Impurities and lattice defects can greatly alter the properties of materials near a structural transition.[3] In all cases, the effects of dislocations on the various quantities characterizing the phase transition have been found to be proportional to the dislocation density n_d.[4,5] However, in materials that contain dislocations that are frozen-in, these effects all become proportional to $n_d^{1/2}$ rather than n_d owing to the formation of a domain wall structure; they are therefore much more pronounced at small densities n_d. In this paper we analyze how dislocation domain walls influence the thermodynamic anomalies, as well as their effects on light scattering and the damping of sound and the soft mode.

2. EQUILIBRIUM VALUE OF THE ORDER PARAMETER FOR $T<T_c$

We consider a phase transition involving the condensation of a soft mode with a wave vector $\mathbf{k}$ in the Brillouin zone. Let a displacement field $\mathbf{v}(\mathbf{r}) = \eta \mathbf{e}_\mathbf{k} \exp(i\mathbf{kr})$ be generated in a perfect crystal below the transition temperature, where $\mathbf{e}_\mathbf{k}$ is the polarization vector for the soft mode and η is the order parameter. The Landau expansion for the free energy density is valid near the transition point:

$$f(\eta) = \frac{a}{2}|\eta|^2 + \frac{b}{4}|\eta|^4 + \frac{1}{2} c_{ij} \frac{\partial \eta^*}{\partial x_i} \frac{\partial \eta}{\partial x_j}. \qquad (1)$$

Here

$$a=a_0\tau, \quad \tau=(T-T_c)/T_c, \quad c_{ij}=c_\perp+(c_\parallel-c_\perp)k_ik_j/k^2$$

(we assume that the system is axisymmetric relative to $\mathbf{k}$). If the transition doubles the lattice period (this is the simplest case), $\mathbf{k}$ is equal to one-half a reciprocal lattice vector and η is real. For arbitrary $\mathbf{k}$ in the Brillouin zone, however, η is in general complex.

A dislocation can be produced in a perfect crystal by slicing it along a half-plane and sliding the edges of the cut relative to one another by an amount equal to the Burgers vector b parallel to the cut. This generates a displacement field $\mathbf{u}(\mathbf{r}^0)$ in the crystal, where the jump discontinuity of $\mathbf{u}(\mathbf{r}^0)$ across the cut is equal to the Burgers vector:

$$u_i(\tilde{x}^0, \tilde{y}^0=+0, \tilde{z}^0)-u_i(\tilde{x}^0, \tilde{y}^0=-0, \tilde{z}^0)=b_i, \quad \tilde{x}^0>0. \qquad (2)$$

The $\tilde{z}^0$ axis is taken parallel to the dislocation, while the $\tilde{x}^0$ axis is parallel to the slipping plane and normal to the dislocation.

If we neglect deformation effects, which are of little importance in our treatment, the free energy density is again given by (1) in the undeformed coordinates $\mathbf{r}^0$. The displacement field generated by the phase transition can be expressed in the form

$$\mathbf{v}(\mathbf{r}^0)=\eta(\mathbf{r}^0)\mathbf{e}_\mathbf{k}e^{i\mathbf{kr}^0}, \qquad (3)$$

where the function $\eta(\mathbf{r}^0)$ is continuous everywhere except at the cut. On the other hand, in terms of the deformed coordinates $\mathbf{r} = \mathbf{r}^0 + \mathbf{u}(\mathbf{r}^0)$ we can write the displacement field as

$$\mathbf{v}(\mathbf{r})=g(\mathbf{r})\mathbf{e}_\mathbf{k}e^{i\mathbf{kr}}, \qquad (3')$$

where $g(\mathbf{r})$ is continuous everywhere. Comparing (3) and (3'), we obtain

$$g(\mathbf{r})=\eta(\mathbf{r}-\mathbf{u})e^{i\mathbf{ku}}.$$

Condition (2) and the continuity of $g(\mathbf{r})$ give rise to the boundary condition

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$$\eta(\tilde{x}, \tilde{y}=+0, \tilde{z}) = e^{i\mathbf{kb}}\eta(\tilde{x}, \tilde{y}=-0, \tilde{z}), \quad \tilde{x}>0 \tag{4}$$

for the order parameter at the cut [the change in $\eta(\mathbf{r})$ over atomic distances can be neglected]. For the case when the lattice period doubles, we have $\mathbf{k}\cdot\mathbf{b} = \pi$ and the boundary condition is

$$\eta(\tilde{x}, \tilde{y}=+0, \tilde{z}) = -\eta(\tilde{x}, \tilde{y}=-0, \tilde{z}), \quad \tilde{x}>0\,. \tag{4'}$$

We stress that the boundary conditions (4), (4') result from our use of undeformed coordinates; the actual displacements of the lattice sites have no singularity across the cut.

The equilibrium distribution of the order parameter for $\tau<0$ is governed by the boundary conditions (4) or (4') together with the familiar equation

$$b(\eta^2-\eta_0^2)\eta - c_c(\beta)\partial^2\eta/\partial x^2 - c_\perp\partial^2\eta/\partial y^2 = 0. \tag{5}$$

Here the x and y axes lie in and normal to the plane defined by the dislocation and the vector $\mathbf{k}$, respectively; $c_c(\beta) = c_\parallel \sin^2\beta + c_\perp\cos^2\beta$, where β is the angle between $\mathbf{k}$ and the dislocation; $\eta_0^2 = |a|/b$.

We consider the case when the lattice period doubles (η real). For distances much greater than the correlation radius $r_c = [(c_c(\beta)c_\perp)^{1/2}|a|]^{1/2}$, the solution has the form of a domain wall with origin at the dislocation (Fig. 1). The order parameter is equal to $-\eta_0$ in region I and $+\eta_0$ in region II; η varies continuously from $-\eta_0$ to $+\eta_0$ inside the domain wall. The equation for the change in η in the wall is

$$b(\eta^2-\eta_0^2)\eta - c_c(\alpha)\partial^2\eta/\partial x_\perp^2 = 0 \tag{6}$$

with boundary conditions

$$\eta \to \pm\eta_0 \quad \text{as} \quad x_\perp \to \pm\infty. \tag{6'}$$

Here the coordinate $x_\perp$ is normal to the wall, and α is the angle between the wall and the vector $\mathbf{k}$. The solution is

$$\eta = \eta_0 \operatorname{th}[x_\perp/2^{1/2}r_c(\alpha)], \tag{7}$$

where $r_c(\alpha) = [c_c(\alpha)/|a|]^{1/2}$. The linear strain on the wall is $\sigma = 2^{3/2}a^2 r_c(\alpha)/3b$. If $c_\perp < c_\parallel$ then the strain is minimized for a wall parallel to $\mathbf{k}$.

When $r \ll r_c$ we need retain only the derivative terms in the left-hand side of Eq. (5). The solution is then

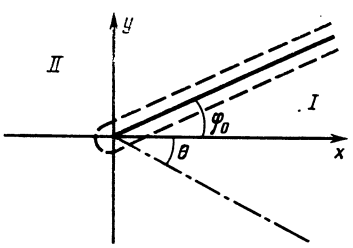

FIG. 1. A dislocation domain wall. The wall is bounded by the dashed curve, while the dashed-and-dotted line shows the plane of the cut. The wall and cut divide the crystal into two regions I and II with order parameter η equal to $-\eta_0$ and $+\eta_0$, respectively.

$$\eta(r, \varphi) = \delta(\varphi)A\eta_0(r/r_c)^{1/2}\{[(1+\Delta\cos 2\varphi)(1+\Delta\cos 2\varphi_0)]^{1/2} - \cos(\varphi-\varphi_0) - \Delta\cos(\varphi+\varphi_0)\}^{1/2}, \tag{8}$$

where r and φ are the polar coordinates in the plane normal to the dislocation, and φ_0 is the angle between the domain wall and the x axis; the constant A is of order unity and can be found by matching (8) with the asymptotic formula for $r \gg r_c$,

$$\delta(\varphi) = \begin{cases} 1, & \varphi_0<\varphi<2\pi-\theta \\ -1, & -\theta<\varphi<\varphi_0 \end{cases},$$

$$\Delta = \frac{(c_\perp - c_\parallel)\sin^2\beta}{c_\perp(1+\cos^2\beta) + c_\parallel\sin^2\beta}.$$

Now let the order parameter be complex. If continuous degeneracy is present then η varies from η_0 to $\exp(i\mathbf{k}\cdot\mathbf{r})\eta_0$ in the entire region around the dislocation. The solution for $r \gg r_c$ describes a vortex:

$$\eta(r, \varphi) = \eta_0 \exp(ikb\psi(\varphi)/2\pi), \tag{9}$$

where

$$\psi(\varphi) = \operatorname{arctg}[(c_c/c_\perp)^{1/2}\operatorname{tg}\varphi] + \gamma(\varphi), \quad -\theta<\varphi<2\pi-\theta,$$
$$\gamma(\varphi) = n\pi, \quad n\pi-\pi/2<\varphi<n\pi+\pi/2.$$

For small distances $r \ll r_c$

$$\eta(r, \varphi) = B\eta_0[(r/r_c)(1+\Delta\cos 2\varphi)]^{\mathbf{kb}/2\pi}\exp(i\mathbf{kb}\psi(\varphi)/2\pi), \tag{9'}$$

where $B \sim 1$.

A similar result was obtained in Ref. 6 for a Heisenberg antiferromagnet with a screw dislocation. The solutions (9) and (9') reduce to the one found in Ref. 6 for $\mathbf{k}\cdot\mathbf{b} = \pi$ and $c_c(\beta) = c_\perp = c_\parallel$. The vortex energy per unit length is

$$E_v = (4\pi)^{-1}(\mathbf{kb})^2(c_c c_\perp)^{1/2}\eta_0^2 \ln(L/r_c),$$

where L is comparable to the distance between the dislocations.

3. CONTRIBUTION FROM DISLOCATION DOMAIN WALLS TO THE THERMODYNAMIC ANOMALIES

We now consider the period doubling case in more detail. If many parallel dislocations are present, a domain wall structure forms in which each wall extends between two dislocations. If the strain on the walls is not too anisotropic, they will extend primarily between adjacent dislocations. If the positions of the dislocations are random and uncorrelated, the distribution of the wall dimensions is given approximately by the distribution function for the minimum distances between the dislocations. Consider an arbitrary dislocation. The probability that the nearest dislocation lies at a distance from l to $l + dl$ away is equal to the product $\exp(-\pi n_d l^2)\cdot 2\pi l n_d dl$, where the first factor is the probability that no dislocations lie within a sphere of radius l, and the second is the probability for a dislocation to lie in a shell of radius l and thickness dl. The distribution function for the nearest-neighbor distances is thus

$$P(l)=2\pi l n_d \exp(-\pi n_d l^2), \quad (10)$$

and we find that $\langle l \rangle = 0.5 n_d^{-1/2}$.

The domain walls are well separated if $r_c n_d^{1/2} \ll 1$. A transition to the phase of higher symmetry occurs when the correlation radius becomes comparable to the average distance between the dislocations, so that the energy associated with the nonuniform structure is comparable to the gain in the local part of the free energy. The dislocations thus decrease the transition temperature by an amount ΔT which can be estimated from the relation $r_c(\Delta T) n_d^{1/2} \sim 1$.

For $r_c n_d^{1/2} \ll 1$ the domain walls give rise to corrections to the thermodynamic quantities. To find the correction to the free energy, we note that the average wall diameter is $\langle l \rangle = 0.5 n_d^{-1/2}$, while the number of walls per unit area is $n_d/2$; hence the correction is

$$\Delta f_w \approx {}^1/_4 n_d^{1/2} \sigma. \quad (11)$$

Since $\sigma \sim f_a r_c$, where f_a is the density for the anomalous part of the free energy, the correction has a stronger singularity as $\tau \to 0$ than is the case for the free energy in a pure substance. However, for $r_c n_d^{1/2} \ll 1$ it remains less than the anomalous part of the free energy. In the Landau region $\Delta f_w \sim |\tau|^{3/2}$, while in the fluctuation region $\Delta f_w \sim |\tau|^{2-\alpha-\nu}$, where α is the critical index for the specific heat and ν is the correlation length.

We next consider the correction to the specific heat

$$\Delta C_w \approx {}^1/_4 n_d^{1/2} T \partial^2 \sigma / \partial T^2.$$

In the Landau region,

$$\Delta C_w \approx 2^{-3/2} n_d^{1/2} a_0^{3/2} c^{1/2} |\tau|^{-1/2} / T_c b,$$

while in the fluctuation region $\Delta C_w \sim |\tau|^{-\alpha-\nu}$. In a perfect crystal the temperature dependence of the specific heat in the Landau region is determined by the fluctuation correction[7]

$$\Delta C_f = 2^{-5/2} k_B a_0^{3/2} |\tau|^{-1/2} / \pi c^{3/2}.$$

If we compare this with the correction due to the domain walls, we find that

$$\frac{\Delta C_w}{\Delta C_f} = \pi \frac{n_d^{1/2}}{k_B T_c} \frac{c^2}{b} \sim \pi d n_d^{1/2} \frac{T_a}{T_c}. \quad (12)$$

Here d is the interatomic distance ($\sim 10^{-7}$ cm) and $T_a = c^2/k_B d b$ is of the order of the atomic temperature ($\sim 10^4$–10^5 K). If $T_c \sim 10^2$ K then the domain walls determine the temperature dependence of the specific heat at densities $n_d \sim 10^7$–10^9 cm^{-2}.

Antiferroelectrics exhibit a dielectric anomaly at the transition point owing to the proximity of the ferroelectric state (see, e.g., Ref. 8). To examine how dislocations influence this anomaly, we expand the free energy density in powers of the polarization P and order parameter in the presence of an electric field E,

$$f(\eta, P) = \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + \frac{c_{ij}}{2}\frac{\partial \eta}{\partial x_i}\frac{\partial \eta}{\partial x_j} + \frac{a_P}{2}P^2 + \frac{c_{Pij}}{2}\frac{\partial P}{\partial x_i}\frac{\partial P}{\partial x_j} - PE + \frac{b_1 \eta^2}{2}P^2, \quad (13)$$

where $a_P = a_{0P}(\tau + \tau_0)$.

The equilibrium distribution P is determined by the equation

$$a_P P + b_1 \eta^2(r) P - c_{Pij} \partial^2 P / \partial x_i \partial x_j = E. \quad (14)$$

For a perfect crystal $P = \text{const}$, and (14) gives $1/\varkappa_0 = a_P + b_1 \eta_0^2$ for the reciprocal of the susceptibility. In the Landau region when $\tau < 0$, $1/\varkappa_0$ increases linearly as the temperature decreases,

$$1/\varkappa_0 = (a_0 b_1 / b - a_{0P}) |\tau| + a_{0P} \tau_0. \quad (15)$$

To estimate the correction to $1/\varkappa_0$ due to domain wall dislocations, we use the equation

$$[a_P + b_1 \eta^2(x_\perp)] P - c_P(\alpha) \partial^2 P / \partial x_\perp^2 = 0 \quad (16)$$

for the change in P near a wall; here $c_P(\alpha) = c_{P\parallel} \sin^2\alpha$ and $c_{P\perp} \cos^2\alpha$, and the function $\eta(x_\perp)$ is given by Eq. (7).

The derivative term in (16) can be neglected in the region $|\tau| \ll \tau_0$, and the dislocation correction is of the form

$$\Delta(1/\varkappa) \approx -n_d^{1/2} r_c b_1 \eta_0^2 \sim -|\tau|^{1/2}. \quad (17)$$

To estimate how the susceptibility behaves in the opposite limit $|\tau| \gg \tau_0$, we make the change of variable $u = x_\perp / 2^{1/2} r_c$. This transforms Eq. (16) into

$$(S_2 - S_1/\mathrm{ch}^2 u) P - \partial^2 P / \partial u^2 = S_1 \varkappa_0 E, \quad (16')$$

where for $\tau \gg \tau_0$ the dimensionless constants $S_1 = 2cb_1/c_P b$ and $S_2 = 2(c/c_P)(b_1/b - a_{0P}/a_0)$ are of order unity. We conclude from (16′) that the additional polarization per unit wall area is given by $\Delta P = C(S_1, S_2) \varkappa_0 r_0 E$, where $C(S_1, S_2) \sim 1$. The correction to the inverse susceptibility when $|\tau| \gg \tau_0$ is therefore

$$\Delta(1/\varkappa) \sim -n_d^{1/2} r_c / \varkappa_0 \sim -|\tau|^{1/2}. \quad (18)$$

The correction in this case also depends on a fractional power of the temperature, but with a different exponent. We have assumed in the above calculation that a ferroelectric transition does not occur on the wall [in order for such a transition to occur, we must have $S_2 > (S_1 - S_2)^2$].

4. LIGHT SCATTERING

Irregularities in the crystal scatter light by producing fluctuations in the dielectric constant ε. The intensity for scattering involving a change in the wave vector by $\mathbf{q}$ is $I \sim \langle |\varepsilon(\mathbf{q})|^2 \rangle$, where $\varepsilon(\mathbf{q})$ is the Fourier component of the dielectric constant. For our qualitative purposes we may neglect the anisotropy, so that

$$\varepsilon = \varepsilon_0 + g\eta^2. \quad (19)$$

We consider scattering by domain walls when the light wavelength λ satisfies $n_d^{-1/2} \gg \lambda \gg r_c$. For visible light, this corresponds to dislocation densities $n_d \lesssim 10^9$ cm^{-2}. The walls scatter independently at these wavelengths, and they perturb ε by an amount

$$\Delta\varepsilon = -g_w \sum_j \delta[(\mathbf{r} - \mathbf{r}_{0j})\mathbf{n}_j] \theta(l_j/2 - |\mathbf{r} - \mathbf{r}_{0j}|), \quad (20)$$

where $g_w = 2^{3/2} g \eta_0^2 r_c$; n_j is the normal to the surface of the

jth wall, which is of length l_j (the walls are parallel to the z axis). The Fourier component of ε is of the form

$$\varepsilon(\mathbf{q}) = -2g_w \sum_j \frac{\sin[(q_x n_{jy} - q_y n_{jx}) l_j/2]}{q_x n_{jy} - q_y n_{jx}} \delta(q_z) \exp(i\mathbf{q}\mathbf{r}_{0j}). \quad (21)$$

Since the component of the wave vector parallel to the wall varies slowly, most of the contribution to the scattering is from walls perpendicular to $\mathbf{q}$ (provided that $q\langle l\rangle \gg 1$, i.e., the scattering angles are not too small). Upon averaging $|\varepsilon(\mathbf{q})|^2$ over l and the directions of the normal n, we obtain the result

$$\langle|\varepsilon(\mathbf{q})|^2\rangle = V g_w^2 n_d^{1/2} \delta(q_z)/2q_\perp, \quad (22)$$

where V is the volume of the illuminated crystal. The total scattering intensity is

$$I_w \sim V(\lambda/2\pi)^2 g_w^2 n_d^{1/2} \ln(\lambda n_d^{1/2}).$$

Since $g_w^2 \sim |\tau|$, the scattering by the dislocation domain walls becomes stronger away from the transition point. The above result may be compared with the intensity

$$I_\rho \sim V(\rho\partial\varepsilon/\partial\rho)^2 k_B T/\Lambda,$$

for scattering by noncritical density fluctuations, where Λ is the elastic modulus. We obtain

$$I_w/I_\rho \sim d n_d^{1/2} \left(\frac{g\eta_0^2}{\rho\,\partial\varepsilon/\partial\rho}\right)^2 \frac{\Lambda d^3}{k_B T} \left(\frac{\lambda r_c}{d}\right)^2. \quad (23)$$

Inserting the estimates

$$g\eta_0^2(\rho\partial\varepsilon/\partial\rho)^{-1} \sim 10^{-1},\ \lambda \sim 10^3 d,\ r_c \sim 10d,$$
$$\Lambda d^3/k_B \sim T_a \sim 10^5\ \text{K},\quad T \sim 10^2\ \text{K},\quad n_d \sim 10^6\ \text{см}^{-2},$$

we find that

$$I_w/I_\rho \sim 10^5.$$

Even at low dislocation densities the walls can thus scatter light much more effectively than the density fluctuations.

5. ABSORPTION OF SOUND

We now consider absorption of a sound wave in a crystal containing dislocation domain walls for which $\lambda_s \gg r_c$, where λ_s is the acoustic wavelength. The sound wave causes the walls to vibrate, resulting in the absorption of energy. We examine the simplest case when the interaction energy for the deformation and order parameter is given by

$$E_{int} = r \int d\mathbf{r}\, \text{div}\, \mathbf{u}\eta^2.$$

We can then write

$$E_{int}^w = r_w \int dr\, \text{div}\, \mathbf{u}\delta[y - v(x,z,t)], \qquad r_w = 2^{1/2}\eta_0^2 r_c r$$

for a deformation interacting with a wall at position y, where $y = v(x,z,t)$. We consider the motion of a wall of length l in the field of a longitudinal acoustic wave $\mathbf{u} = \mathbf{u}_0 \exp[i(\mathbf{qr} - \omega t)]$. If the interaction is weak the perturbation of the sound wave may be neglected to lowest order, and the wall displacement $v(x,z,t) = v(x)\exp([i(q_z z - \omega t)]$ obeys the equation

$$(-\rho_w\omega^2 + i\gamma_w\omega + \sigma q_z^2 - \sigma\partial^2/\partial x^2) v(x) = r_w q_y(\mathbf{qu}) \exp(iq_x x) \quad (24)$$

with the boundary conditions $v(0) = v(l) = 0$.

We have

$$\rho_w = 2^{1/2}\rho_\eta \eta_0^2/r_c, \quad \gamma_w = 2^{1/2}\gamma_\eta \eta_0^2/r_c,$$

in the Landau region, where ρ_η and γ_η are the effective mass and the damping constant for the soft mode. The power absorbed per unit length of wall is given by

$$P_w(l,\mathbf{q}) = \frac{1}{2} r_w q_y (q u_0)\, \omega \int_0^l dx\, \text{Im}[\exp(iq_x x) v^*(x)]. \quad (25)$$

The energy absorbed by the wall per unit volume per unit time is

$$\dot{E} = {}^1/_2 n_d \langle P(l, q_\perp \cos\varphi, q_\perp \sin\varphi, q_z)\rangle_{l,\varphi}.$$

The averaging is carried out over the angle φ between the projection of the acoustic wave vector $\mathbf{q}$ and the z axis, and over the length l [with the weight function (10)]. We neglect the anisotropy in σ, ρ_w, γ_w and solve Eq. (24) by taking Fourier transforms. Inserting the solution into (25) yields the following expression for the inverse acoustic relaxation time $1/\tau_s = \dot{E}/\rho\omega^2 u_0^2$:

$$\frac{1}{\tau_s} = \frac{r_w^2 n_d}{8\rho\rho_w} \sum_{n=1}^{\infty} \left\langle \frac{(1/\tau_w) l q_\perp^2 \sin^2\varphi\, |a_n(q_\perp l \cos\varphi)|^2}{\{\omega^2 - v_w^2[q_z^2 + (\pi n/l)^2]\}^2 + \omega^2/\tau_w^2} \right\rangle_{\varphi,l}. \quad (26)$$

Here $v_w = (\sigma/\rho_w)^{1/2}$ and $1/\tau_w = \gamma_w/\rho_w$ are the propagation velocity of the wall oscillations and the inverse relaxation time, and the

$$a_n(ql) = 2\pi n[1 - (-1)^n \exp iql][(\pi n)^2 - (ql)^2]^{-1}$$

are the coefficients in the expansion of $\exp(iqx)$ in terms of the harmonics $\sin(\pi n x/l)$.

If $1/\tau_w \gg v_w n_d^{1/2}$ and the frequency satisfies $1/\tau_w \gg \omega \gg \tau_w v_w^2 n_d$, one can derive the result

$$\frac{1}{\tau_s} = \frac{r_w^2 \tau_w n_d^{1/2} q^2}{16\rho\rho_w v_s^2} \sin^2\alpha_s, \quad (27)$$

where v_s is the speed of sound and α_s is the angle between the acoustic wave vector and the dislocations. In the Landau region, expression (27) can be recast as

$$\frac{1}{\tau_s} = \frac{(2n_d)^{1/2} r^2 \eta_0^2 r_c^3 q^2}{4\rho\gamma_2 v_s^2} \sin^2\alpha_s. \quad (28)$$

We now compare this result with the case of absorption by the Landau-Khalatnikov relaxation mechanism.[9] The sound wave perturbs the order parameter and acoustic energy is absorbed for finite relaxation times, because η is unable to adjust back to its equilibrium value. The inverse relaxation time corresponding to this mechanism is

$$1/\tau_{L\text{-}K} = 2r^2 q^2 \eta_0^2 \gamma_\eta/\rho a^2. \quad (29)$$

Comparison of (28) and (29) yields

$$\frac{\tau_{L\text{-}K}}{\tau_s} = \frac{(2n_d)^{1/2} r_c^3 a^2}{8\gamma_\eta^2 v_s^2} \sim n_d^{1/2} r_c (\omega_\eta \tau_\eta)^2 \left(\frac{v_\eta}{v_s}\right)^2, \quad (30)$$

where $v_\eta^2 = c/\rho_\eta$ ($v_\eta \sim v_s$), and $\omega_\eta = (a/\rho_\eta)^{1/2}$ and $\tau_\eta = \rho_\eta/\gamma_\eta$ are the frequency and relaxation time for the soft mode. The result (30) shows that the absorption by the domain walls can exceed that due to relaxation when $\omega_\eta \tau_\eta \gg 1$ (i.e., sufficiently far from the transition point).

At low temperatures there is a region in which the inequality $1/\tau_w \ll v_w n_d^{1/2}$ holds. Here the absorption is resonant—sound at frequency ω is absorbed primarily by walls whose dimensions are close to the resonance values $l_{res}(n)$:

$$\omega^2 = v_w^2 [q_z^2 + (\pi n/l_{pes}(n))^2]. \quad (31)$$

The absorption is greatest at frequencies roughly equal to $\omega_0 = \pi v_w n_d^{1/2}$. If the walls are soft (so that $v_w \ll v_s$), we have $q_\perp l \ll 1$ in the region of maximum absorption. Calculations of the absorption using this inequality lead to the result

$$\frac{1}{\tau_s} = \frac{3 r_w^2 n_d^{1/2} \omega}{2\rho_w \rho v_s^4} f\left(\frac{\omega}{\omega_0}\right), \quad (32)$$

where

$$f(x) = x^{-3} \sum_{n=0}^{\infty} (2n+1) \exp[-\pi(2n+1)^2 x^{-2}]$$

is given approximately by

$$f(x) = \begin{cases} \exp(-\pi/x^2)/x^3, & x \ll 1 \\ 1/4\pi x, & x \gg 1 \end{cases}.$$

For small and large x (see Fig. 2). With the estimates

$$\rho_\eta \sim \rho, \; r_c \sim 10d, \; \eta_0 \sim 0{,}1d, \; r\eta_0^2/\rho v_s^2 \sim 10^{-2},$$

we obtain $1/\tau_s \omega \sim 10^{-3}$ in the region of strongest absorption if we set $n_d \sim 10^8$ cm^{-2}.

6. DAMPING OF THE SOFT MODE

We now consider the oscillations in the order parameter caused by the domain walls. When defects are present, the oscillations in η heat the material nonuniformly and are damped due to heat transfer between different regions of the crystal.[3] The equations of motion for the order parameter near a domain wall (including temperature fluctuations) are

$$-\rho_\eta \omega^2 \eta + i\omega\gamma_\eta \eta + |a| \left[2 - \frac{3}{\mathrm{ch}^2(x_\perp/2^{1/2} r_c)}\right]\eta - c_{ij} \frac{\partial^2 \eta}{\partial x_i \partial x_j} + \frac{a_0}{T_c} \eta_0 T' = 0, \quad (33)$$

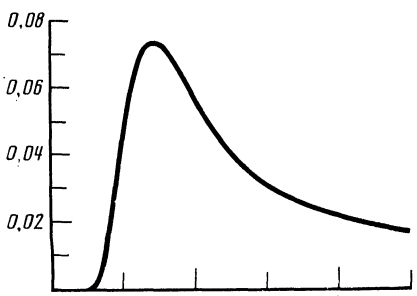

FIG. 2. The function $f(x)$ determining the shape of the resonant acoustic absorption curve.

$$i\omega C_\eta T' - i\omega a_0 \eta_0(x_\perp)\eta = \varkappa \Delta T', \quad (34)$$

where C_η is the specific heat for $\eta = \text{const}$ and $\varkappa$ is the thermal conductivity. The expression

$$\dot{E} = -\frac{1}{2}\int d\mathbf{r} [\gamma_\eta \omega^2 \eta\eta^* + a_0 T_c^{-1} \eta_0(\mathbf{r}) \mathrm{Im}(\eta^* T')] \quad (35)$$

for the absorbed power can be derived from Eq. (33). The potential describing the interaction between the order parameter and domain wall is nonreflecting. The phase shift during passage of an order parameter wave with wave vector $\mathbf{q}$ tends to zero as $\mathbf{q} \to 0$ (Ref. 10). For this reason, the form of the eigenmode with $\mathbf{q} = 0$ changes only near a wall; we will neglect this and take η to be independent of $\mathbf{r}$. Edge effects near the ends of the walls will also be ignored. Since η changes sign near the wall and the amount of heating is proportional to $\eta_0(x_\perp)\eta$, the temperature change will have opposite signs on either side of the wall. Since $(\varkappa/C_\eta \omega_\eta)^{1/2} \gg r_c$ everywhere except in a narrow temperature interval near the transition point, we can replace $\eta_0(x_\perp)$ by a step function. The change in temperature near the wall is then given by

$$T' = \frac{a_0 \eta_0 \eta}{C_\eta} \{1 - \exp[-(iC_\eta \omega_\eta/\varkappa)^{1/2} |x_\perp|]\}. \quad (36)$$

Substitution into Eq. (35) gives

$$\gamma_d = 2^{-3/2} n_d^{1/2} \frac{a_0^2}{T_c} \left(\frac{\varkappa}{C_\eta \omega_\eta}\right)^{1/2} \frac{\eta_0^2}{C_\eta \omega_\eta} \quad (37)$$

for the contribution from the domain walls to the effective damping constant $\gamma_\eta = \rho_\eta \dot{E}/E$. If we use the estimates $C_\eta \sim k_B^4 T^3 (\hbar \sim v_s)^{-3}$ and $\varkappa \sim k_B T_a v_s / T d^2$ for the phonon specific heat and thermal conductivity (they are valid for T comparable to the Debye temperature T_D), we obtain the following result for the dimensionless ratio $\gamma_d/\rho_\eta \omega_\eta = 1/\tau_d \omega_\eta$:

$$1/\tau_d \omega_\eta \sim n_d^{1/2} d \tau^{-1/4} (T_a^3/T_c^2 T)^{1/2} (T_D/T)^{9/2}. \quad (38)$$

Setting $n_d \sim 10^8$ cm^{-2}, $T \sim T_c \sim T_D \sim 10^2$ K, and $\tau \sim 1$, we get the estimate $1/\tau_d \omega_\eta \sim 1$. This mechanism can thus damp the soft mode even at frequencies quite far from the transition point.

The above result may be compared with the damping due to anharmonic effects[8]:

$$1/\tau_\eta \omega_\eta = A(k_B T/\hbar\omega_\eta) + B(k_B T/\hbar\omega_\eta)^2, \quad A \sim 10^{-2}, \quad B \sim 10^{-3}.$$

This expression is more singular than $1/\tau_d \omega_\eta$ as $\tau \to 0$. However, for the above parameter values and $\tau \sim 1$, the damping by the domain walls is two orders of magnitude greater. It should be noted that the contribution from the domain walls to the damping constant, which determines the relaxation absorption of sound for $T \approx T_c$ [Eq. (29)], differs greatly from (37). The perturbation of the order parameter by the acoustic wave can be described by adding a driving force $f(x_\perp) = r\eta_0(x_\perp)$ div $\mathbf{u}$ to the right-hand side of (33). Because this force changes sign near the wall, so does the associated change in the order parameter, and the even eigenmode considered above is not excited by the wave. The

damping constant for the forced oscillations therefore differs greatly from the damping constant for the eigenmode. In our case the amplitude of the heat source, which is proportional to $\eta_0(x_\perp)\eta(x_\perp)$ [Eq. (34)], is spatially constant except within distances $\langle r_c$ from the wall. For $r_c \ll \varkappa/C_\eta\omega$ the temperature distribution is of the form

$$T' \sim \frac{i\omega a_0\eta_0\eta r_c}{(i\omega\varkappa C_\eta)^{1/2}} \exp\left[-\left(\frac{i\omega C_\eta}{\varkappa}\right)^{1/2} |x_\perp|\right].$$

Substitution into (35) then yields the estimate

$$\tilde{\gamma}_d \sim \frac{a_0^2}{T_c}\frac{n_d^{1/2}\eta_0^2 r_c^2}{(\omega C_\eta\varkappa)^{1/2}} \sim \frac{a_0^2 c n_d^{1/2}}{bT_c(\omega C_\eta\varkappa)^{1/2}}. \tag{39}$$

This result is valid when $\omega \gg n_d\varkappa/C_\eta$, i.e., when the heat transfer occurs independently for each wall. At low frequencies $\omega \ll n_d\varkappa/C_\eta$ the departure of the temperature from its equilibrium value is expressible as

$$T' = a_0\overline{\eta_0(\mathbf{r})\eta(\mathbf{r})}/C_\eta + T'', \tag{40}$$

where the bar denotes a spatial average; $T'' \ll a_0\,\overline{\eta_0\eta}/C_\eta$ obeys the equation

$$\varkappa\Delta T'' = -ia_0\omega\delta(\eta_0\eta),$$

where $\delta(\eta_0\eta)$ is the deviation of $\eta_0\eta$ from its average value. We have the estimate

$$T'' \sim ia_0\omega\overline{\eta_0\eta}r_c t(\mathbf{r})/n_d^{1/2}\varkappa,$$

where $t(\mathbf{r}) \sim 1$, $\overline{t(\mathbf{r})} = 0$. Substituting this into Eq. (35), we obtain

$$\tilde{\gamma}_d \sim \frac{a_0^2}{T_c}\frac{\eta_0^2 r_c^2}{\varkappa} \sim \frac{a_0^2 c}{bT_c\varkappa}. \tag{41}$$

At low frequencies the effective damping constant for the forced oscillations is thus independent of the dislocation density. For $T \sim T_D$ and $n_d \sim 10^8$ cm^{-2}, the transition from (39) to (41) occurs at frequencies $\omega \sim 10^8$–10^9 s^{-1}.

7. CONCLUSIONS

We have used a simple model to analyze how dislocations affect the properties of phase transitions that are accompanied by an increase in the volume of the elementary cell. The model treats a phase transition of the displacement type in which a single soft mode condenses. The situation for real crystals is frequently more complicated. For example, in lead zirconate (an antiferroelectric), several soft modes condense simultaneously, and the elementary cell for the low-temperature phase contains eight elementary cells for the high-temperature phase. In nonintrinsic ferroelectrics, the order parameter has two components. There are also materials (such as ammonium dihydrophosphate, ADP) in which the period increases as a result of an order-disorder transition. Although the specific models for the interaction of the order parameter with dislocations differ, in all cases dislocations are responsible for domain wall formation when $T < T_c$, and the results found above remain qualitatively correct. Above the transition point, the order parameter interacts with the dislocations either through the deformation field[4] or because the order parameter is distorted at the centers of defects.[3,5] For $T > T_c$, all the effects involved in the interaction are proportional to the dislocation density n_d, while for $T < T_c$ they are proportional to $n_d^{1/2}$, owing to the formation of domain walls in this case. It would be extremely interesting to have comprehensive experimental data on how plastic deformation alters the properties of phase transitions that increase the volume of the elementary cell.

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