Change of defect structure and the resultant anomalies in the properties of substances near phase-transition points

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The defect-induced anomalies of a number of characteristics of matter near second-order phase transition points in various substances are investigated theoretically. The temperature dependences of the thermodynamic quantities, of the light-scattering intensity, of the sound-absorption coefficient, and of the soft-mode damping constant are considered. The anomalies near the transition point (T_c) are attributed to the evolution with temperature of the defect-induced static distortions of the matrix, which correspond to an order parameter η. The independent-defect approximation is used, wherein the correlation radius of the order parameter is smaller than the average distance between defects. The structure distortions caused by the defects are described in a continual approximation on the basis of a phenomenological theory of phase transitions. For intrinsic ferroelectrics and ferroelastics, account is taken, in this case, of the long-range forces due to the macroscopic and electric and elastic fields. The value η_0 of the structure distortion in the core of the defect is determined in self-consistent manner and likewise turns out to be temperature dependent. At an appreciable value of η_0, the anomalies of the properties of the substance in the investigated temperature region are qualitatively similar to the known fluctuation anomalies, although their temperature dependences differ in character. Estimates show that the anomalies connected with defects can exceed the fluctuation anomalies even at ordinary defect concentrations ($\sim 10^{18}$ cm^{-3}). The temperature dependence of η_0 can lead, in particular, to a local phase transition with change of structure of the defect (the appearance of defect distortions corresponding to η). This phenomenon, which has already been discussed in the literature, is also considered within the framework of the employed approach.

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INTRODUCTION

The influence of defects on the properties of substances near the phase transition points has been the subject of a large number of theoretical studies. In the development of the theory, principal attention has been paid so far to renormalization of the critical exponents and to the "smearing" of the critical singularities (see, e.g., Refs. 1–4), which take place in the temperature region where the correlation radius r_c of the order parameter η exceeds the average distance r_s between defects. In addition, the perturbations introduced by the defects were as a rule assumed to be small. At the same time, not enough attention has been paid to the simpler case, when $r_c < r_s$ and the defects can be regarded as weakly interacting, yet it is precisely this case which in our opinion is of interest when it comes to the interpretation of most experimental data.

The influence of defects on the properties of matter is particularly great near the second-order phase transition temperature T_c. The structure of matter near T_c becomes "soft" to distortions corresponding to η. In particular, the characteristic length r_c over which the parameter η specified at a certain point is varied, becomes infinite at $\tau \equiv (T-T_c)/T_c = 0$. Consequently, the dimension of the region perturbed by the defects also increases if the distortions caused by the defects include some that correspond to the parameter η. These arguments, which have been developed in a number of papers,[5-7] were advanced also in a somewhat different form (in the language of lattice dynamics) by other workers.[8,9] Strong temperature changes of the properties of matter near the phase-transition point can lead also to a jumplike defect-structure realignment having the character of a unique "local phase transition." Examples of such a restructuring can be the following: spontaneous appearance of a magnetic moment at a paramagnetic impurity,[10,11] the onset of an ordered region near a dislocation in a solid solution,[12] a jumplike increase of the magnetic moment near a vacancy when solid ^{3}He is magnetized,[13] spontaneous appearance of a current of a magnetic flux in a Josephson junction with paramagnetic impurities,[14] etc. Other papers dealing with the structure of defects and with their influence on the properties of matter in the vicinity of the phase transition can also be cited.[15-20]

In this paper we investigate, within the framework of the phenomenological theory, the changes of the structure of defects near phase-transition points in various substances. The results are used to consider the defect-induced anomalies of certain properties of matter.

The qualitative character of these anomalies can frequently be understood from elementary considerations. Thus the increase of the dimensions of the region of the medium distorted by the defect leads apparently to an increase of the cross section for the scattering of light by a single defect, and consequently to an increase of the intensity of the scattering due to fluctuations of the defect concentration.[6] Changes of the defect structure should lead also to a temperature dependence of the defect contribution to the thermodynamic quantities and to the kinetic coefficients. Since the defects can be regarded as something like "frozen" fluctuations of η, one should expect the anomalies due to defects to be similar to known fluctuation anomalies.[21] The presence of defects should, in particular, increase the sound absorption by the symmetrical phase as $\tau \to 0$. In fact,

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for pure matter the anomaly of sound absorption in the asymmetrical phase is connected both with relaxation of the order parameter and with its thermal fluctuations, while in the symmetrical phase it is connected only with the thermal fluctuations of η. The presence of defects, which can be regarded as nucleation centers of an asymmetrical phase, gives rise to formation of regions of relaxation absorption at $\tau > 0$, and the size of this region increases as $\tau \to 0$, thus leading to an additional increase of the absorption of the sound. Similar arguments can be advanced also with respect to the damping of the oscillations of the order parameter—the "soft mode." In the asymmetrical phase of pure matter, in contrast to the symmetrical phase, these oscillations are accompanied by temperature oscillations. In the vicinity of the defect, the temperature oscillations can occur also in a symmetrical phase, and it is this which causes the additional damping of the oscillations of η as a result of thermal conductivity.

In the present paper, the substance is described in a continual approximation, and the presence of defects is taken into account in the boundary conditions of the equations of the continuous medium. These conditions are specified on the boundary of the "core" of the defect, i.e., in a spatial region with characteristic dimension *d*, inside of which the continuous-medium approximation is not valid. We emphasize that in the continual theory the distortions introduced by the defects are usually taken to be the elastic (acoustic) deformations,[22] since the changes of the other internal parameters (such as "optical" deformations of the crystal) fall off as a rule approximately within interatomic distances. However, as already noted, near the phase-transition point the characteristic state of the falloff of the distortions that correspond to the order parameter η increases substantially, so that these distortions can also be described in the continuous-medium approximation. These are precisely the distortions of interest to us here. In addition, since we are considering the case $r_c < r_s$, the defects are assumed to be noninteracting, and their contribution to the various physical quantities are assumed to be additive. A similar approach was used to treat defects such as the sample surface and extraneous particles in liquid helium.[23-25]

Section 1 deals with the possible types of boundary conditions on the core of the defect and with a determination of the corresponding distributions of $\eta(\mathbf{r})$ near the defect, as well as with the change of the free energy due to one defect. In Sec. 2 is considered the contribution of the defects to the anomalies of the thermodynamic quantities near second-order phase transition points under the assumption that the value of $\eta(\mathbf{r})$ on the boundary of the core of the defect does not depend on the temperature. In Secs. 3 and 4, under the same assumption, we calculate the contribution of the defects to anomalies of light scattering and of sound absorption, as well as to damping of the soft mode. In Sec. 5 is formulated a more general approach to the problem, wherein the boundary conditions at the core of the defect are no longer regarded as fixed, and are determined in a self-consistent manner. This procedure makes it possible not only to justify and refine the results of the preceding sections, but also to consider the question of possible changes produced in the state of the defect core by strong temperature variations of the properties of the matrix. Examples of model calculations of the phenomenological constants used in the theory and characterizing the core of the defects are discussed in the Appendix.

1. CONTRIBUTION OF THE DEFECTS TO THE FREE ENERGY OF A SUBSTANCE

We consider first a point defect and assume the boundary of its core to be spherical. In this case, for a single-component order parameter, the boundary conditions on the core reduce to specifying the function $\eta(\theta, \varphi; d)$ on a sphere of radius *d*. Expanding $\eta(\theta, \varphi; d)$ in spherical functions, we can formulate the simplest types of boundary conditions, assuming one of the terms of this series to be different from zero. For our purposes it suffices to consider the first two terms of the expansion; this is equivalent to specifying on the boundary of the core the order parameter $\eta = \eta_0$ (defect in state *S*) or its derivative $(\partial\eta/\partial z)_d = \eta_1/d$ (defect in state *P*). Of course, η_0 and η_1 can differ from zero simultaneously (defect in state *SP*). Possible types of boundary conditions on the core of the defect are illustrated in Fig. 1 with a ferroelectric transition of the displacive type as an example. The boundary conditions for linear (one-dimensional) defects such as dislocations, as well as for planar (two-dimensional) defects such as twin boundaries, are similarly formulated. In the former case one specifies the function $\eta(\varphi, d)$ on a cylindrical surface of radius *d*, and in the latter the values of η_1 and η_2 on the planes that bound the core of the defect. Linear defects in the states *S* and *P* correspond respectively to the first $(m = 0)$ and second $(m = 1)$ terms of the expansion of the function $\eta(\varphi, d)$ in powers of $\cos m\varphi$. A planar defect in state *S* corresponds to the boundary condition $\eta_1 = \eta_2 = \eta_0$, and in the state *P* to the condition $\eta_1 = -\eta_2$. It is obvious that a planar defect can be only in states *S*, *P*, or *SP*.

We assume first that the defect is in the state *S*. We represent the free energy of the substance with such a defect in the form

$$\Phi = \int\limits_{V-V_0} \left[\varphi(\eta) + \frac{D}{2}(\nabla\eta)^2 - h\eta \right] dV + [f(\eta_0) - h\eta_0]V_0, \qquad (1.1)$$

where the first term is the free energy of the matrix and the second is the free energy of the core of the de-

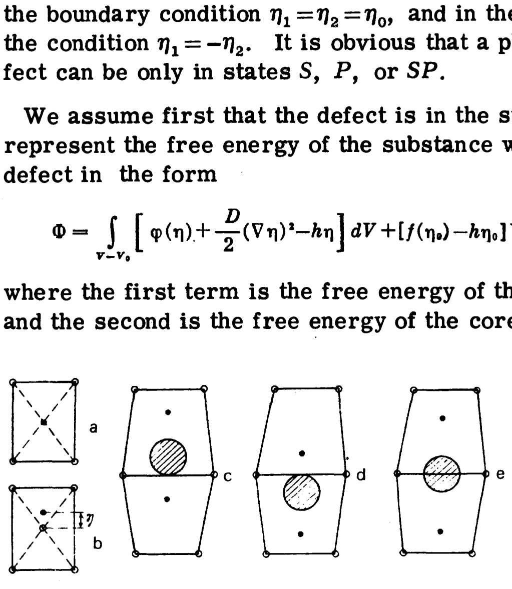

FIG. 1. Schematic representation of the distortions of the structure of a crystal in the vicinity of point defects of various types: a) unit cell of symmetrical phase, b) unit cell of asymmetrical phase, c) defect in the state $S(\eta_0 > 0)$, d) defect in the state $S(\eta_0 < 0)$, e) defect in the state *P*.

fect with volume V_0; h is the generalized field conjugate to the order parameter. The microscopic meaning of the function $f(\eta_0)$ for different models of the defect is discussed in the Appendix.

By varying expression (1.1) with respect to $\eta(\mathbf{r})$ at a given η_0, we obtain an equation that describes the distribution $\eta(\mathbf{r})$

$$D\nabla^2\eta=\varphi'(\eta)-h, \tag{1.2}$$

with boundary conditions

$$\eta(r=d)=\eta_0, \quad \eta(r\to\infty)=\eta_\infty, \tag{1.3}$$

where the quantity η_∞ is determined from the equality

$$\varphi'(\eta_\infty)=h. \tag{1.4}$$

The function $\varphi(\eta)$, as usual, is expressed in the form of a series

$$\varphi(\eta)=\varphi_0+\frac{A}{2}\eta^2+\frac{B}{4}\eta^4+\frac{C}{6}\eta^6+\ldots. \tag{1.5}$$

In the Landau theory of second-order phase transitions, the only ones considered here, we have $A=A_0\tau$, $B, C=\text{const}>0$. Expression (1.5) with altered temperature dependences of the coefficients can actually be used also in the scaling region, where the Landau theory is not applicable.[24] It will be convenient hereafter to expand the function $\varphi(\eta)$ in powers of $(\eta-\eta_\infty)$. Substituting this series in expression (1.1) and (1.2), we get

$$\Phi=[\varphi(\eta_\infty)-h\eta_\infty](V-V_0)+\int\limits_{V-V_0}\Big\{\frac{1}{2!}\varphi''(\eta_\infty)(\eta-\eta_\infty)^2$$
$$+\frac{1}{3!}\varphi'''(\eta_\infty)(\eta-\eta_\infty)^3+\ldots+\frac{D}{2}[\nabla(\eta-\eta_\infty)]^2\Big\}dV+[f(\eta_0)-h\eta_0]V_0, \tag{1.6}$$

$$D\nabla^2(\eta-\eta_\infty)=\varphi''(\eta_\infty)(\eta-\eta_\infty)+\frac{1}{2!}\varphi'''(\eta_\infty)(\eta-\eta_\infty)^2+\ldots. \tag{1.7}$$

Integrating in (1.6) by parts the term containing $\nabla(\eta-\eta_\infty)$ and using (1.1), we obtain for the integral in (1.6)

$$\Phi_1=-\int\limits_{V-V_0}\left[\frac{1}{2\cdot 3!}\varphi'''(\eta_\infty)(\eta-\eta_\infty)^3+\frac{1}{4!}\varphi^{IV}(\eta_\infty)(\eta-\eta_\infty)^4+\ldots\right]dV$$
$$-\int\frac{D}{2}(\eta-\eta_\infty)\nabla(\eta-\eta_\infty)dS. \tag{1.8}$$

Equation (1.7) cannot be solved exactly in three- and two-dimensional cases. In the linear approximation for point defects in the S state, the $\eta(\mathbf{r})$ distribution is described by the well known Ornstein–Zernike function

$$\eta(r)-\eta_\infty=(\eta_0-\eta_\infty)\frac{d}{r}\exp\left(\frac{d-r}{r_c}\right), \tag{1.9}$$

where the correlation radius r_c is given by

$$r_c^2=D/\varphi''(\eta_\infty). \tag{1.10}$$

For Φ_1 we obtain in the same approximation

$$\Phi_1=\Phi_1^{(0)}=2\pi Dd\left(1+\frac{d}{r_c}\right)(\eta_0-\eta_\infty)^2. \tag{1.11}$$

The $\eta(\mathbf{r})$ distribution near the point defect in the state P can be obtained, by differentiating (1.9) with respect to z and satisfying the boundary condition $\eta(\theta, r=d)=\eta_1\cos\theta$, in the form

$$\eta(\mathbf{r})=\eta_\infty\left[1-\frac{d}{r}\exp\left(\frac{d-r}{r_c}\right)\right]-\eta_1\frac{d^2\cos\theta}{1+d/r_c}\frac{\partial}{\partial r}\left[\frac{1}{r}\exp\left(\frac{d-r}{r_c}\right)\right]. \tag{1.12}$$

In this case

$$\Phi_1^{(0)}=\frac{4\pi}{3}Dd\eta_1^2\left[1+\frac{d^2}{2r_c^2(1+d/r_c)}\right]+2\pi Dd\eta_\infty^2\left(1+\frac{d}{r_c}\right). \tag{1.13}$$

By iteration we can calculate the corrections to $\Phi_1^{(0)}$, which arise when account is taken of the nonlinear terms in (1.7). For a defect in the same S, calculation of the first correction to $\Phi_1^{(0)}$

$$\Phi_1^{(1)}\approx\frac{4\pi}{3!}(\eta_0-\eta_\infty)^3\varphi'''(\eta_\infty)d^3\ln\frac{d}{r_c}+\frac{4\pi}{4!}(\eta_0-\eta_\infty)^4\varphi^{IV}(\eta_\infty)d^3 \tag{1.14}$$

makes it possible to obtain a criterion for the applicability of the linear approximation:

$$\left(\frac{Bd^2\eta_0^2}{D}\ln\frac{d}{r_c}\right)^{1/2}\approx\eta_0/\eta^*\ll 1. \tag{1.15}$$

Analysis shows that when the condition (1.15) is satisfied, the corrections are small not only for Φ_1, but also for the derivatives of Φ_1 with respect to τ and h. We note that in the region of applicability of the Landau theory the quantity $\eta^*\equiv(D/Bd^2)^{1/2}$ has the meaning of the atomic (maximum possible) value of the order parameter, corresponding to total ordering, to displacement of the sublattices by an atomic distance, etc., i.e., the linear approximation can be used here even for relatively "strong" defects. In the scaling region, the dependence of η^* on τ is given by $\eta^*\sim|\tau|^{\nu-\beta}$. Usually $\nu-\beta\approx\beta\approx\frac{1}{3}$,[21,26] and consequently the condition (1.15) is practically always satisfied in the scaling region.

For a linear defect in the state S, the distribution $\eta(\mathbf{r})$ and the value of Φ_1, both calculated in first-order approximation, are given by the expressions (ρ is the distance to the axis of the defect)

$$\eta-\eta_\infty=(\eta_0-\eta_\infty)\frac{K_0(\rho/r_c)}{K_0(d/r_c)}, \tag{1.16}$$

$$\frac{\Phi_1}{L}=\frac{\pi Dd}{r_c}(\eta_0-\eta_\infty)^2\frac{K_1(d/r_c)}{K_0(d/r_c)}\approx\pi D(\eta_0-\eta_\infty)^2\ln^{-1}\left(\frac{\pi r_c}{2d}\right), \tag{1.17}$$

where L is the length of the effect, while $K_0(z)$ and $K_1(z)=-dK_0/dz$ are cylindrical functions of imaginary argument. It is known that as $z\to\infty$ we have

$$K_0(z)\approx\left(\frac{\pi}{2z}\right)^{1/2}e^{-z}, \tag{1.18a}$$

and as $z\to 0$

$$K_0(z)\approx-\ln\frac{z}{2}. \tag{1.18b}$$

The criterion for the applicability of the linear approximation is much more stringent here:

$$(Br_c^2\eta_0\eta_\infty/D)^{1/2}\approx(\eta_0/\eta_\infty)^{1/2}\ll 1. \tag{1.19}$$

Thus, this approximation is valid only for sufficiently "weak" linear defects.

In the case of planar defects, the linear approximation is likewise valid only at $(\eta_0/\eta_\infty)^{1/2}<1$. However, the distribution $\eta(x)$ and the quantity Φ_1 can in this case be calculated exactly, since Eq. (1.7) has as its first integral

$$D\left(\frac{d\eta}{dx}\right)^2=(\eta-\eta_\infty)^2R(\eta,\eta_\infty),$$

$$R(\eta,\eta_\infty)=\varphi''(\eta_\infty)+\frac{2}{3!}\varphi'''(\eta_\infty)(\eta-\eta_\infty)+\frac{2}{4!}\varphi''''(\eta_\infty)(\eta-\eta_\infty)^2+\ldots. \tag{1.20}$$

From this and from (1.18) we get

$$x=D^{1/2}\int_{\eta}^{\eta_0}dt\,(t-\eta_\infty)^{-1}R^{-1/2}(t,\eta_\infty), \tag{1.21}$$

$$\Phi_1=2D^{1/2}\int_{\eta_\infty}^{\eta_0}dt\,(t-\eta_\infty)R^{1/2}(t,\eta_\infty). \tag{1.22}$$

In a nonsymmetrical phase these formulas are valid only at $\eta_0>-\eta_\infty$. In the opposite case (for weak fields, $h\to 0$), Eq. (1.20) has no solution that satisfies the boundary condition $\eta(x\to\infty)=\eta_\infty$. This means that at $\eta_0\leqslant-\eta_\infty$ the approximation of non-interacting defects is incorrect.

In intrinsic ferroelectrics and ferroelastics, and also in ferromagnets, a change of $\eta(\mathbf{r})$ is accompanied by the appearance of long-range forces—electric, elastic, or magnetic, respectively. For ferromagnets this circumstance can be disregarded down to very small values of $|\tau|$, but for uniaxial ferroelectrics and ferroelastics it influences the results strongly. In the case of an extremely anisotropic ferroelectric with one spontaneous-polarization axis $z(\eta\equiv P_z)$ the $P_z(r)$ distribution for a point defect in the state S was obtained previously in the linear approximation.[7] Using this result we get

$$\Phi_1\approx\frac{1}{2}(P_{z0}-P_{z\infty})^2\left[\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{1}{\varphi''(P_{z\infty})+Dk^2+4\pi n_z^2}\right]^{-1}$$
$$\approx 2\pi Dd(P_{z0}-P_{z\infty})^2\left\{1+\frac{\pi^{1/2}d}{D^{1/2}}\left[1-\frac{D}{8\pi r_c^2}\ln\frac{\varphi''(P_{z\infty})}{16\pi}\right]\right\}, \tag{1.23}$$

where $n_z=k_z/k$, and the integration is over the wave vectors $|\mathbf{k}|<k_{\max}$. Introduction of $k_{\max}=\pi/2d$ is analogous to the introduction of the defect core radius d.

For triaxial ferroelectrics, using the result of Ref. 27, we have

$$\Phi_1\approx\frac{1}{2}(P_{z0}-P_{z\infty})^2\left\{\int d\mathbf{k}[\varphi''(P_{z\infty})+Dk^2+4\pi(1-n_z^2)]\right.$$
$$\left.\times[(2\pi)^3(\varphi''(P_{z\infty})+Dk^2)(\varphi''(P_{z\infty})+Dk^2+4\pi)]^{-1}\right\}^{-1}$$
$$\approx 2\pi Dd(P_{z0}-P_{z\infty})^2\left[1+\frac{2d}{3\pi}\left(\frac{\varphi''(P_{z\infty})}{D}\right)^{1/2}\right]. \tag{1.24}$$

The direction of the polarization P_{z0} at the defect coincides here with the direction of the z axis.

In an intrinsic ferroelectric, the order parameter is one of the components of the strain tensor $(\eta\equiv u_{xy})$. Using the results of Ref. 28, we get

$$\Phi_1=\frac{1}{2}(u_{xy0}-u_{xy\infty})^2\left\{\int dk[[(n_x^2-n_y^2)+n_z^2(n_x^2+n_y^2)](\lambda+2\mu)\right.$$
$$+\mu(n_x^2+n_y^2)][(2\pi)^3[\varphi''(u_{xy\infty})+Dk^2+4\mu n_z^2$$
$$\left.+4n_x^2n_y^2\mu(\lambda+\mu)/(\lambda+2\mu)]]^{-1}\right\}^{-1}. \tag{1.25}$$

Here λ and μ are Lamé coefficients, and φ'' denotes the elastic modulus corresponding to u_{xy}, it being assumed that the expression for the energy corresponding to the remaining components of the elastic strain tensor is the same as in the isotropic case.

A detailed analysis has shown that the criterion (1.15) of the applicability of the employed approximation remains physically in force also for point defects of S type in systems with long-range action.

2. CONTRIBUTION OF DEFECTS TO THE ANOMALIES OF THE THERMODYNAMIC QUANTITIES

It will be shown later (see Sec. 5) that to obtain approximate results and estimates, we can assume the order parameter η_0 at the core of the defect to be fixed near the phase transition point at a value $\eta_0=\eta_0(\tau=0)\equiv\eta_{00}$.

It is then possible to leave out of (1.6) the temperature-independent term $f(\eta_0)V_0$. In addition, in the first term of this expression we can neglect the quantity V_0 compared with V (omitting V_0, we neglect the obvious change produced in the anomalies by the decrease in the fraction of the volume participating in the phase transition when defects are introduced into the medium). For the contribution of a point defect in a state S to the free energy of the system we then obtain

$$\Phi_d\approx\Phi_1=2\pi Dd(1+d/r_c)(\eta_0-\eta_\infty)^2. \tag{2.1}$$

Differentiating (2.1) with respect to h and τ (with account taken of the implicit dependence of r_c and η_∞ on h and τ) we obtain (at a field $h=0$) the contribution of the defects to the order parameter $\bar\eta$ averaged over the volume, to the generalized susceptibility χ corresponding to the order parameter, and to the specific heat c

$$\bar\eta_d=\frac{4\pi dr_c^2}{V}\left[\eta_0-\eta_\infty-\frac{1}{4}\frac{d}{r_c}\frac{\varphi'''(\eta_\infty)}{\varphi''(\eta_\infty)}\eta_0^2\right], \tag{2.2}$$

$$\chi_d^{-1}=-\frac{4\pi Dd}{V}\left\{(\eta_0-\eta_\infty)\frac{\varphi'''(\eta_\infty)}{\varphi''(\eta_\infty)}+\frac{\eta_0^2d}{4r_c}\left[\frac{\varphi''''}{\varphi''}-\frac{3}{2}\left(\frac{\varphi'''}{\varphi''}\right)^2\right]+1\right\} \tag{2.3}$$

$$c_d=-\frac{2\pi Dd}{T_cV}\left\{\eta_0^2\left(\frac{d}{r_c}\right)_\tau''-2\eta_0\left[\left(\frac{d\eta_\infty}{r_c}\right)_\tau''\right.\right.$$
$$\left.\left.+\frac{d}{r_c}(\eta_\infty)_\tau''\right]+\left(\frac{d}{r_c}\eta_\infty\right)_\tau''+(\eta_\infty^2)_\tau''\right\}. \tag{2.4}$$

The lower index τ in (2.4) means that the differentiation is with respect to τ.

The results for other types of defects, and also for defects in systems with long-range forces, will not be presented completely. They can be obtained by differentiating the corresponding expressions for Φ_1. For comparison we shall later on mention only briefly some of these results.

It is obvious that η_0 can be of either sign. Let us discuss the contribution of the defects to the anomalies of the thermodynamic quantities in three very simple cases: a) frozen-in random defects, when the value of η_0 at each defect is fixed, and the concentrations of defects with opposite signs of η_0 are equal; b) frozen-in "polarized" defects, when the sign of η_0 is the same for all defects; c) "polarization reversing" defects, when the defect can undergo transitions between states with $\pm|\eta_0|$. The first case can be realized, for example, in a crystal grown at $T>T_c$, the second in a single-domain crystal that remains for a long enough time at $T<T_c$.

a) The contribution of the frozen-in random defects to the thermodynamic quantities can be obtained from formulas (2.1)–(2.4), in which we leave out the terms linear in η_0, and by multiplying by the number of defects. Assume first that the Landau theory is valid in the entire region of applicability of our approach (i.e., at $Nr_c^3 < 1$, where N is the defect concentration). For a second-order phase transition far from the tricritical point, the temperature dependence of $\bar{\eta}$, χ, and c can be represented in the form

$$\bar{\eta}_{fcd}^2 = \frac{A_0}{B}\left\{|\tau| - \frac{4\pi NDd}{A_0}\left[1 + \frac{3}{2}\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{r_c}{d}\right]\right\}, \tag{2.5}$$

$$\chi_{fcd}^{-1} = A_0\left\{\tau + \frac{4\pi NDd}{A_0}\left[1 + \frac{3}{2}\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{r_c}{d}\right]\right\}, \quad \tau>0 \tag{2.6a}$$

$$\chi_{fcd}^{-1} = 2A_0\left\{|\tau| - \frac{4\pi NDd}{A_0}\left[1 + \frac{21}{8}\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{r_c}{d}\right]\right\}, \quad \tau<0, \tag{2.6b}$$

$$c_{fcd}/\Delta c = \pi N r_c^3 (\eta_0/\eta^*)^2, \quad \tau>0 \tag{2.7a}$$

$$c_{fcd}/\Delta c = 1 + 4\pi N\left\{r_c^3\left(\frac{\eta_0}{\eta^*}\right)^2\left[1 - 2\frac{\eta_\infty}{\eta_0}\frac{r_c}{d} - 3\left(\frac{\eta_\infty}{\eta_0}\right)^2\right] + 4d^3\left[\ln\frac{r_c}{d} - \zeta + \frac{DC}{2B^2d^2}\right]\right\}, \quad \tau<0. \tag{2.7b}$$

Here $\Delta c = A_0^2/2BT_c$ is the jump of the specific heat at the phase transition point, as given by the Landau theory, and $\zeta \approx 1.5$.

Figure 2 shows the temperature dependence of $\bar{\eta}^2$. In a region not too close to the phase-transition point, when

$$\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{r_c}{d} < 1,$$

this dependence is linear, just as in a pure substance. Extrapolating this straight line to the intercept with the abscissa axis, we obtain the renormalization of the transition temperature:

$$\Delta\tau = \frac{T_c - T_c'}{T_c} = \frac{4\pi NDd}{A_0}. \tag{2.8}$$

A similar renormalization of T_c follows from formulas (2.6) (Fig. 2b). At $N \approx 10^{18}$ cm^{-3}, $d \approx 10^{-7}$ cm and $(D/A_0)^{1/2} \approx 10^{-7}$ cm (values estimated, for example, for SrTiO$_3$, Ref. 29), $\Delta\tau$ amounts to ~10^{-2}, and agrees in order of magnitude with experiment.[30,31] At

$$\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{r_c}{d} \approx 1$$

the deviation from the linear temperature dependence of $\bar{\eta}^2$ and χ^{-1} become noticeable, as is clear from Fig. 2 (curves 2). However, the values of these deviations, even at the limit of validity of the theory ($Nr_c^3 \approx 1$), can be appreciable only for strong defects with $(\eta_0/\eta^*)^2 \approx (Nd^3)^{1/3}$, i.e., at $N \approx 10^{18}$ cm^{-3} and $(\eta_0/\eta^*)^2 \approx 10^{-2} - 10^{-1}$.

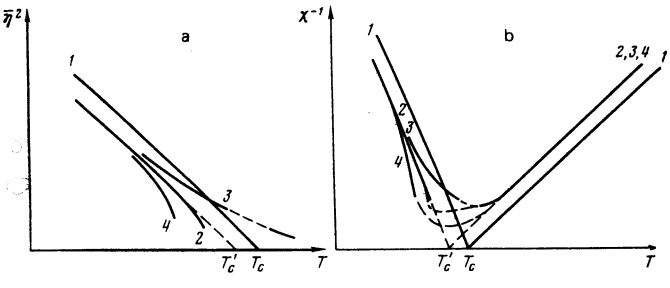

FIG. 2. Temperature dependence of the square of the order parameter (a) and of the reciprocal generalized susceptibility corresponding to the order parameter (b) in the region of applicability of the Landau theory: 1—in the absence of defects; 2—in systems with frozen-in random defects; 3—in systems with frozen-in "polarized" defects, when the signs of η_0 and η_∞ coincide; 4—in systems with frozen-in "polarized" defects when η_0 and η_∞ have different signs.

The character of the temperature dependence of the specific heat c is also determined essentially by the value of the parameter η_0. The contribution of strong defects ($\eta_0 \sim \eta^* \gg 3\eta_\infty$) to the specific heat, as follows from (2.7), increases when the phase-transition point is approached from either the symmetrical or the asymmetrical phase, in accordance with the law $c_{fcd} \propto |\tau|^{-3/2}$. At the boundary of the region of applicability of the employed approximation ($Nr_c^3 \approx 1$), c_{fcd} reaches a value of the order of the jump of the specific heat Δc in the pure substance (Fig. 3, curve 3). A dependence of this type is frequently observed in experiments, but is usually attributed to thermal fluctuations of the order parameter. The contribution of the latter at $T > T_c$ is given in first approximation by the formula[32]

$$c_f = \frac{k_B A_0^{3/2}}{16\pi D^{3/2}\tau^{1/2}}. \tag{2.9}$$

From (2.3) and (2.9) we obtain for c_{fcd}/c_f at $Nr_c^3 = 1$

$$\frac{c_{fcd}}{c_f} = 16\pi^2\left(\frac{\eta_0}{\eta^*}\right)^2 \frac{A_0^2}{4B}\frac{r_{c0}^3}{k_BT_c}(Nr_{c0}^3)^{1/3} \approx 4\pi^2\left(\frac{\eta_0}{\eta^*}\right)^2\left(\frac{T^*}{T_c}\right)(Nd^3)^{1/3}, \tag{2.10}$$

where $T^* = D^2/Bdk_B$ is of the order of the atomic temperature (~10^4–10^5 K). For $N \approx 10^{18}$ cm^{-3}, $d \approx 10^{-7}$ cm, $\eta_0/\eta^* \approx 10^{-1}$, $T_c \approx 10^2$ K the ratio is $c_{fcd}/c_f \approx 1$–10, i.e., it is quite probable that in many cases the observed anomalies of the thermodynamic quantities, which are usually attributed to thermal fluctuations, are actually due to defects. For sufficiently weak defects ($N_0^2 \lesssim N^{2/3}D/B$), as follows from (2.7), the heat capacity decreases monotonically with increasing temperature (curve 2 of Fig. 3), i.e., the presence of defects leads in this case only to a smearing of the jump of the specific heat. In the intermediate case the function $c_{fcd}(T)$ (curve 4 in Fig. 3) has a minimum. The last term in (2.7b) determines the specific-heat-discontinuity renormalization due to the defects. We note that part of this renormalization is connected with the term $\frac{1}{6}C\eta^6$ in (1.5), which is usually not taken into account in the analysis of second-order phase transitions that are far from the tricritical point.[1)] On the other hand, the other part arises when the first correction (1.14) to Φ_d is differentiated. We emphasize that all defects con-

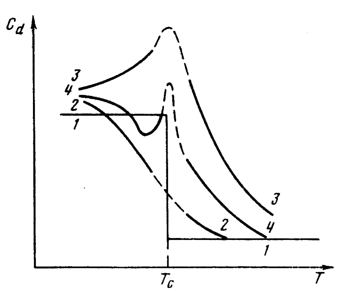

FIG. 3. Temperature dependence of the specific heat in the region of applicability of the Landau theory: 1—in the absence of defects; in systems with frozen-in random defects: 2—for weak defects, 3—for strong defects, 4—for the intermediate case.

tribute to the renormalization of the discontinuity, including defects in the state P, since the magnitude of the renormalization does not depend on η_0. At $A_0C/B^2 \sim 10$, as is the case for triglycin sulfate[33] and at $NdD/A_0 \sim 10^{-3}$, the renormalization of the specific heat is of the order of Δc. The experimental data[34] show that the jump of the specific heat in triglycin sulfate is several time larger than the value given by the Landau–Ginzburg–Devonshire theory. It is not excluded that this discrepancy is connected with the presence of defects. The same temperature dependence as c_{fcd} is obviously possessed also by contributions of the defects to such thermodynamic quantities as the compressibility and the coefficient of thermal expansion. To obtain the corresponding expressions it is necessary to multiply the expression for c_{fcd} in the first case by $T_c^{-1}(dT_c/dP)^2$ and in the second by $T_c^{-1}dT_c/dP$. In other words, the Pippard relations remain valid for these quantities.[35]

Formulas (2.2)–(2.4) make it possible to analyze the behavior of the thermodynamic quantities in the similarity region, where the Landau theory is not applicable. In this case

$$\eta_\infty \sim (-\tau)^\beta,\ \varphi''(\eta_\infty) \sim |\tau|^{-\gamma},\ \varphi'''(\eta_\infty) \sim |\tau|^{\gamma-\beta},$$
$$\varphi''''(\eta_\infty) \sim |\tau|^{\gamma-2\beta},\ r_c \sim |\tau|^{-\nu},$$

where $\nu = (\gamma + 2\beta)/3$ and usually $\beta \approx \frac{1}{3}$, $\gamma \approx \frac{4}{3}$.[21,26] The contribution of the defects to the quantity $\bar{\eta}^2$ varies now like $\bar{\eta}^2_{fcd} - \eta^2_\infty \sim |\tau|^{-2/3(\gamma-\beta)}$. The influence of the defects on the temperature dependence of the reciprocal susceptibility χ^{-1} in this region reduces in practice to a shift of the corresponding curves along the ordinate axis, either upward (at $\tau > 0$) or downward (at $\tau < 0$), by an amount that does not depend on the temperature and is proportional to the defect concentration. This change of $\chi^{-1}(T)$ can be interpreted also as some lowering of the transition temperature. We note that the correction terms to formulas (2.2) and (2.3), which contain η_0^2, do not change this result in fact, inasmuch as they are practically independent of the temperature in the critical region. The contribution of the defects to the specific heat has a stronger temperature dependence in the critical region ($c_{fcd} \sim |\tau|^{\nu-2}$ at $\eta_0 \neq 0$ and $c_{fcd} \sim |\tau|^{2\beta-2}$ at $\eta_0 = 0$), than in the region where the Landau theory is valid, and its sign is positive also at $\tau < 0$, regardless of the value of η_0.

The thermodynamic anomalies due to the presence of other types of defects have a number of singularities compared with those considered above. For linear defects (it is possible to analyze here only the case of weak defects with $\eta_0 - \eta_\infty \leq \eta_\infty$) in the nonsymmetrical phase we have $c_{fcd} \propto |\tau|^{2-2\beta} \ln^{-2}|\tau|$, i.e., the presence of these defects leads to a maximum on the temperature dependence of the specific heat. On the contrary, in the case of planar defects in the region where the Landau theory is valid, only a smearing of the discontinuity of the specific heat takes place. Point defects in the P state also lead to a smearing of the specific-heat discontinuity, and the corresponding contribution to the specific heat (just as the contribution of the planar defects) is proportional to $|\tau|^{-1/2}$, i.e., it has above T_c has the same temperature dependence as the contribution of the fluctuations. The ratio c_{fcd}/c_f in the case of defects of P type is equal to

$$c_{fcd}/c_f \approx 16\pi^2 Nd^3 (\eta_1/\eta^*)^2 (T^*/T_c).$$

At $\eta_1 = \eta^*$, $Nd^3 \approx 10^{-4}$ and $T^*/T_c \approx 10^2$ this ratio is of the order of unity. As to the contribution of P defects to $\bar{\eta}^2$ and χ^{-1}, it reduces to a renormalization of the transition temperature, similar to (2.8), without deviations from the linear relations. For intrinsic uniaxial ferroelectrics and intrinsic ferroelastics, the contribution of S-type defects to the specific heat (at $\eta_0 \neq 0$) changes like $|\tau|^{-1}$ and $|\tau|^{-1/2}$, respectively. These temperature dependences are stronger than the fluctuation dependences ($c_f \sim \ln|\tau|^{-1}$ and $c_f \sim c_1 - c_2\tau^{1/2}$, Refs. 36, 37, 28).

b) For a system with frozen-in polarized defects we obtain from (2.2)–(2.4)

$$\bar{\eta}_{fpd} = \bar{\eta}_{fcd} + \frac{4\pi NDd\eta_0}{\varphi''(\eta_\infty)}, \tag{2.11}$$

$$\chi^{-1}_{fpd} = \chi^{-1}_{fcd} + 4\pi NDd\eta_0 \frac{\varphi'''(\eta_\infty)}{\varphi''(\eta_\infty)}, \tag{2.12}$$

$$c_{fpd} = c_{fcd} - 8\pi N r_c^3 \frac{r_c}{d} \frac{\eta_0\eta_\infty}{(\eta^*)^2} \Delta c, \quad \tau<0, \tag{2.13a}$$

$$c_{fpd} = c_{fcd},\ \tau>0. \tag{2.13b}$$

The second terms in (2.11) and (2.12) can be interpreted as the changes of $\bar{\eta}$ and χ^{-1} under the influence of the effective "field" $\tilde{h} = 4\pi NDd\eta_0$, produced by the defects. For ferroelectric phase transitions at $N \approx 10^{18}$ cm^{-3} this would correspond to an electric field $E \approx 10^4 - 10^5$ V/cm. We note that the appearance of an additional term in expression (2.13a) for c_{fpd} at $\tau < 0$ cannot be attributed to the presence of such a field, since c depends on h only in quadratic fashion.

The dependence of $\bar{\eta}_{fpd}$ on the temperature is shown schematically in Fig. 2 for the cases when η_0 and η_∞ are of equal (curve 3) and of opposite sign (curve 4). The sign of η_∞, as seen from (1.4), is determined by the field h, which can be easily realized in experiment in the case of intrinsic ferroelectric, magnetic, and ferroelastic transitions. The field h can be specified also in all other cases, when the transition parameter is a tensor, i.e., the phase transition is not accompanied by a change in the translational symmetry of the substance. Thus, for example, for the $\alpha \rightleftharpoons \beta$ structure transition in quartz, the role of the field h can be played by the gradients of the elastic-stress components, which have the same transformation properties as η.

It follows from (2.13) that the character of the temperature dependence of the specific heat at $\tau < 0$ also depends substantially on the ratio of the signs of the parameters η_0 and η_∞. When the signs agree, the curve for the specific heat is similar to curve 3 of Fig. 3, and if the signs are opposite, it is similar to curve 2 of the same figure.

We note that the condition for applicability of the approximation of the indepent defects in our case is somewhat more stringent than for random defects. In fact, as follows from (2.11), this condition take the form $2^{3/2}\pi N r_c^3 \eta_0/\eta^* < 1$, whereas for random defects the factor η_0/η^* is raised to the second power in the corresponding inequality.

c) Proceeding now to consider polarization-reversing defects, we denote by $N_+ = \frac{1}{2}(N + \Delta N)$ and $N_- = \frac{1}{2}(N - \Delta N)$ the concentrations of the defects in states with different signs of η_0. The value of ΔN in the state of thermodynamic equilibrium must be determined from the condition that the free energy be a minimum. The expression for the density of the free energy of the system at $\Delta N/N \ll 1$ can be written in the form

$$\Phi_{sd}(h, T, \Delta N) = \varphi(\eta_\infty) - h\eta_\infty + \frac{N}{2}(\Phi_1^{(+)} + \Phi_1^{(-)}) + \frac{\Delta N}{2}(\Phi_1^{(+)} - \Phi_1^{(-)}) + \frac{k_BT}{2} N\left(\frac{\Delta N}{N}\right)^2, \tag{2.14}$$

where the plus and minus signs correspond to different signs of η_0 in (1.11). The last term in (2.14) takes into account the entropy of a system of N_+ and N_- independent defects.

Minimizing (2.14) with respect to ΔN, we obtain for the equilibrium value of ΔN_e

$$\Delta N_e = \frac{N}{2k_BT}(\Phi_1^{(+)} - \Phi_1^{(-)}) = \frac{4\pi Dd(1 + d/r_c)N\eta_0\eta_\infty}{k_BT}. \tag{2.15}$$

Substitution of (2.15) in (2.14) yields

$$\Phi_{sd}(N, T) = \varphi(\eta_\infty) - h\eta_\infty + 2\pi NDd\left(1 + \frac{d}{r_c}\right) \times \left\{\eta_0^2 + \eta_\infty^2\left[1 - \frac{4\pi Dd(1 + d/r_c)\eta_0^2}{k_BT}\right]\right\}. \tag{2.16}$$

This expression differs from the corresponding expression in the case of frozen-in random defects in that the square brackets contain a second term. The expressions for $\bar{\eta}^2$ and χ^{-1} are obtained in this case by replacing unity in the round brackets of (2.5) and (2.6) by $(1 - 4\pi Dd\eta_0^2/K_BT)$, and then the temperature dependences of $\bar{\eta}^2$ and χ^{-1} are similar to those shown in Fig. 2, but with a different effective "shift" of the transition temperature

$$\Delta\tau_{sd} = \frac{T_c - T_c'}{T_c} = \frac{4\pi NDd}{A_0}\left(1 - \frac{4\pi Dd\eta_0^2}{k_BT_c}\right). \tag{2.17}$$

If

$$\eta_0^2 > \frac{k_BT_c}{4\pi Dd} \approx \frac{(\eta^*)^2}{4\pi}\frac{T_c}{T^*}$$

the sign of $\Delta\tau_{sd}$ is negative, i.e., the temperature of the transition shifts upwards relative to the temperature of transition in the pure substance. For $N \approx 10^{18}$ cm^{-3}, $d \approx (D/A_0)^{1/2} \approx 10^{-7}$ cm, $T_c/T^* \approx 10^{-2}$, $\eta_0/\eta^* \approx 10^{-1}$ it follows from (2.17) that $\Delta\tau \approx 0.1$.

The rise of the transition temperature when the crystal has polarization-reversing impurities was considered previously[17] on the basis of microscopic models and for an opposite limiting case ($Nr_c^3 \gg 1$). The physical cause of the shift of the transition point in these two cases is the same, but the results, naturally, can differ quantitatively.

3. ANOMALIES OF LIGHT SCATTERING BY DEFECTS

Light scattering is due, as is well known, to disturbance of the optical homogeneity of the medium. The dielectric tensor ε_{ij} in the optical band is in this case different at different points of the medium, i.e., it undergoes spatially inhomogeneous fluctuations. When light is scattered by defects, the inhomogeneities of ε_{ij} are due to fluctuations of the defect concentration. In the temperature interval of interest to us, there is practically no diffusion of the defects and the fluctuations of N can be regarded as independent of the temperature. At the same time, the fluctuations of ε_{ij} increase as $\tau \to 0$, owing to the temperature dependence of the contribution made to ε_{ij} by individual defects.[5] We shall assume dependence of ε_{ij} on η to be quadratic (a linear dependence of some components of ε_{ij} on η obtains in the case of structural transitions only for intrinsic ferroelastics, which will be considered separately). Leaving out the tensor indices, we have

$$\varepsilon = \varepsilon_0 + a\eta^2. \tag{3.1}$$

The contribution of interest to us, that of the defect to the permittivity of the crystal, is given by

$$\frac{1}{V}a\int \eta^2(\mathbf{r})\,d\mathbf{r}.$$

Using the corresponding formulas for the distribution $\eta(\mathbf{r})$ in the case of point defects in the state S (Refs. 7, 27, 28), we get

$$\Delta\varepsilon(\mathbf{r}) = \varepsilon_d N(\mathbf{r}), \tag{3.2}$$

where

$$\varepsilon_d \approx 2\pi ad^2(\eta_0 - \eta_\infty)^2 r_c, \tag{3.3}$$

$$\varepsilon_d \approx \frac{1}{2}a(\pi D)^{1/2}d^2(P_{z0} - P_{z\infty})^2\left|\ln\frac{\varphi''(P_{z\infty})}{16\pi}\right|, \tag{3.4}$$

$$\varepsilon_d \approx \pi ad^2(P_{z0} - P_{z\infty})^2 r_c, \tag{3.5}$$

$$\varepsilon_d \approx a(u_{xy0} - u_{xy\infty})^2(C_1 - C_2r_c^{-1}), \quad C_1,\ C_2 = \text{const}, \tag{3.6}$$

respectively, for systems in the absence of long-range forces, uniaxial ferroelectrics, triaxial ferroelectrics, and ferroelastics.

It is known that the intensity of the scattered light is

$$I \sim V^2\langle|\Delta\varepsilon(\mathbf{q})|^2\rangle, \tag{3.7}$$

where V is the volume of the system, $\mathbf{q}$ is the difference between the wave vectors of the incident and scattered light, the symbol $\langle\ldots\rangle$ denotes statistical averaging, and $\Delta\varepsilon(\mathbf{q})$ is the spatial Fourier component of the function $\Delta\varepsilon(\mathbf{r}) = \varepsilon(\mathbf{r}) - \langle\varepsilon\rangle$. Taking (3.2) into account we obtain

$$I \sim V^2\varepsilon_d^2\langle|\Delta N(\mathbf{q})|^2\rangle. \tag{3.8}$$

For frozen-in randomly displaced defects[21] we have

$$\langle|\Delta N(\mathbf{q})|^2\rangle = \frac{N}{V} \tag{3.9}$$

and

$$I \sim \varepsilon_d^2 VN. \tag{3.10}$$

As seen from (3.10), the temperature dependence of I is determined by the function $\varepsilon_d(\tau)$. Consequently, for point defects in all the crystals, with the exception of uniaxial ferroelectrics and intrinsic ferroelastics, we have

$$I \sim r_c^2 \sim |\tau|^{-2\nu}. \tag{3.11}$$

For uniaxial ferroelectrics

$$I \sim \ln^2(r_c/d) \sim \ln^2|\tau|, \tag{3.12}$$

and for intrinsic ferroelastics

$$I \sim (C_1 - C_2r_c^{-1})^2 \to \text{const} \tag{3.13}$$

as $\tau \to 0$.

We can obtain similarly formulas for linear and planar defects. We recall that all the presented formulas are valid at $Nr_c^3 \ll 1$. It is natural to expect that, starting with $Nr_c^3 \approx 1$, the growth of the intensity will become weaker. In the case of intrinsic ferroelastics, the contribution of the defects to the intensity of the light scattering due to fluctuations of those ε_{ij} components which depend linearly on η, is given as before by formula (3.10), where ε_e is given by

$$\varepsilon_d = a_1 \int [\eta(\mathbf{r}) - \eta_\infty] dV = a_1 \frac{\bar{\eta} - \eta_\infty}{N}. \tag{3.14}$$

Calculating $\bar{\eta}$ for this case, we find that

$$I \sim (C_1' - C_2' r_c^{-1} - C_3 \eta_\infty)^2 \to \mathrm{const} \tag{3.15}$$

as $\tau \to 0$.

The intensity of the scattering of x rays and neutrons by defects can be calculated in analogy with the intensity of the scattering of the light waves, assuming that $\Delta\varepsilon \sim \Delta\eta$. The corresponding expressions for the scattering intensity can be easily obtained by using formulas (3.10), (3.14), and the expressions for $\bar{\eta}$.2)

The scattering intensity of spectral distribution given by formulas (3.11)–(3.13) takes the form of a central peak whose width is determined by the reciprocal time of diffusion of the considered defects. For most phase transitions in solids, the diffusion time can be regarded as practically infinite, therefore the width of the central peak in these cases is essentially zero. It has been shown[17] that because of thermal jumps of polarization-reversing defects between states with opposite signs of η_0 the spectrum of the scattered light acquires a central peak with a width determined by the characteristic time of the thermal jumps. We note that the total intensity of this scattering does not exceed the total intensity of the scattering by thermal fluctuations of η, which is proportional to T^2 at $\tau > 0$ (Ref. 38), and is consequently quite small for low-temperature phase transitions. At the same time, the intensity of the scattering of light by defects, given by formulas (3.11)–(3.13), is determined not by the temperature of the transition but only by the concentration of the defects and by the proximity of the system to the phase-transition point.

It follows from (3.2)–(3.6) that the contribution of the defects to the refractive index of the crystal increases when the phase-transition point is approached from either phase. However, owing to the temperature dependence of the refractive index of the matrix, the total refractive index of the crystal remains a monotonic function of the temperature. A reduction of the results of several experiments[39,40] has shown that the temperature dependence of the refractive index of the crystal can be represented as a sum of two curves, one corresponding to $\varepsilon(\eta_\infty)$, and the other having a maximum at the phase-transition point. This maximum can in principle be connected with either the thermal fluctuations of η or with the presence of defects. In the latter case, using the corresponding experimental data and formulas (3.11)–(3.13), we can determine directly the intensities of the light scattering by the defects.

The maximum intensity of the scattering by defects $I_{\max}$ can be estimated by putting $Nr_c^3 = 1$ in formula (3.10). We then obtain for the ratio of the intensity of the scattering by defects to the intensity I_ρ of the noncritical scattering by thermal fluctuations of the density ρ (Ref. 6)

$$\frac{I_{max}}{I_\rho} \approx (4\pi)^2 \left[\frac{a\eta_0^2}{\rho(\partial\varepsilon/\partial\rho)}\right]^2 \frac{\lambda d^3}{k_B T_c} (Nd^3)^{1/3}, \tag{3.16}$$

where λ is the modulus of elasticity. If we assume

$$a\eta_0^2/\rho(\partial\varepsilon/\partial\rho) \approx 10^{-1}, \quad d \approx 10^{-8}-10^{-7}\,\mathrm{cm}, \quad N \approx 10^{18}\,\mathrm{cm}^{-3},$$
$$\lambda \approx 10^{11}-10^{12}\,\mathrm{erg}\cdot\mathrm{cm}^{-3}, \quad T = (10-10^3)\,\mathrm{K},$$

then

$$I_{max}/I_\rho \sim 10^{-2}-10^5. \tag{3.17}$$

Thus, the presence of defects in the crystal can in principle be the cause of the large increase of the scattering intensity of light near the phase-transition point. It is possible that this is precisely the reason for the scattering anomaly observed in $\mathrm{SrTiO_3}$.[41,31]

4. CONTRIBUTION OF DEFECTS TO THE ANOMALY OF THE KINETIC COEFFICIENTS

In the calculation of the contribution of defects to the anomaly of the kinetic coefficients, the corresponding equations of motion must take into account the spatial inhomogeneity introduced by the defects in $\eta(\mathbf{r})$. We do so using as example the analysis of the anomaly of sound absorption and of the friction coefficient, which enters in the equation of motion for η (we shall arbitrarily speak henceforth of the attentuation constant of the soft mode).

a) *Sound absorption coefficient.* We consider the simplest case of a longitudinal sound wave in an elastic anisotropic medium. The equation that describes the propagation of such a wave, with allowance for the ensuing changes of $\eta(\mathbf{r}, t)$, is of the form

$$\rho\ddot{u} = \Lambda \frac{\partial^2 u}{\partial x^2} + 2r \frac{\partial^2 \eta_e}{\partial x^2} \eta' + 4r \frac{\partial \eta_e}{\partial x} \frac{\partial \eta'}{\partial x} + 2r\eta_e \frac{\partial^2 \eta'}{\partial x^2}, \tag{4.1}$$

where $\mu \equiv u_{xx}$ is the longitudinal deformation, η' is the change of the order parameter in the sound wave, $\eta_e(\mathbf{r})$ is its equilibrium value (defined by the formulas of Sec. 1 for an isolated defect), Λ is the elastic modulus that determines the velocity of the longitudinal wave, and r is the coefficient in the relation

$$\sigma_{xx} = \Lambda u_{xx} + r\eta^2. \tag{4.2}$$

Changing over in (4.1) to the Fourier components $u(\mathbf{k}, \omega)$ and $\eta'(\mathbf{k}, \omega)$, we have

$$\rho\omega^2 u(\mathbf{q}, \omega) = \Lambda q^2 u(\mathbf{q}, \omega) + 2rq^2 \sum_{\mathbf{k}} \eta_e(\mathbf{q}-\mathbf{k}) \eta'(\mathbf{k}, \omega), \tag{4.3}$$

where $\mathbf{q}$ and ω are the wave vector and frequency of the sound wave. In the region of low (acoustic) frequencies, the equation of motion for $\eta'(\mathbf{r}, t)$ can be written in the form

$$\gamma\dot{\eta} + \varphi''(\eta_e(\mathbf{r}))\eta' - D\nabla^2\eta' + 2r\eta_e(\mathbf{r})u = 0. \tag{4.4}$$

Retaining, just as in the calculation of the thermodynamic quantities, only the terms of the lowest order in the ratio η_0/η^* and changing over to Fourier components, we get

$$[-i\omega\gamma+\varphi''(\eta_\infty)+Dk^2]\eta'(\mathbf{k},\omega)+2r\eta_e(\mathbf{k}-\mathbf{q})u(\mathbf{q},\omega)=0, \tag{4.5}$$

where the second term takes into account only one Fourier component of the function $u(\mathbf{r}, t)$. From (4.5) we get $\eta'(\mathbf{k}, \omega)$. Substituting (4.5) in (4.3), we obtain an expression for the contribution of the defects to the complex elastic modulus

$$\tilde{\Lambda}_d(\mathbf{q},\omega)=\Lambda-4r^2\sum_{\mathbf{k}}\frac{|\eta_e(\mathbf{q}-\mathbf{k})|^2}{\varphi''(\eta_\infty)+Dk^2-i\omega\gamma}. \tag{4.6}$$

The imaginary part of $\tilde{\Lambda}_d(q=0, \omega)$, which determines the sound absorption coefficient, is equal to $(V=1)$

$$\mathrm{Im}\,\tilde{\Lambda}_d(q=0,\omega)=\frac{16\pi\gamma\omega r^2}{(2\pi)^3}\int\frac{|\eta_e(\mathbf{k})|^2k^2dk}{\varphi''(\eta_\infty)+Dk^2}$$
$$=\pi\gamma\omega\left(\frac{r\eta_0 d}{D}\right)^2 Nr_c^5=2\pi\frac{\omega}{\Omega_0}\Delta\Lambda\left(\frac{\eta_0}{\eta^*}\right)^2 Nr_c^3\sim|\tau|^{-5/2}\omega, \tag{4.7}$$

where $\Omega_0=\varphi''(\eta_\infty)/\gamma$ is the relaxation frequency of the order parameter, and $\Delta\Lambda\equiv r^2/2B$ is the "jump" of the modulus Λ in a phase transition in the pure substance.

It is of interest to compare expression (4.7) with the formulas for the contribution of the thermal fluctuations to the quantity[42] $\mathrm{Im}\Lambda(q=0, \omega)$

$$\mathrm{Im}\,\Lambda_f(q=0,\omega)=\frac{\Delta\Lambda}{2^{7/2}\pi}\frac{\omega}{\Omega_0}\frac{k_BT_cBr_c}{D^2}\sim|\tau|^{-3/2}\omega. \tag{4.8}$$

For the ratio of these two contributions we have

$$\frac{\mathrm{Im}\,\tilde{\Lambda}_d(q=0,\omega)}{\mathrm{Im}\,\Lambda_f(q=0,\omega)}=2^{9/2}\pi^2Ndr_c^2\frac{D\eta_0^2}{k_BT_c}. \tag{4.9}$$

At the limit of applicability of our analysis ($Nr_c^3\approx1$) at $Nd^3\approx10^{-4}$ this ratio is $(T^*/T_c)(\eta_0/\eta^*)^2$, i.e., for sufficiently strong defects their contribution to the anomaly of the sound absorption near the phase-transition point can become predominant. We note that all the formulas written above are suitable both in the region of applicability of the Landau theory and in the critical region. In the latter case $\mathrm{Im}\Lambda_d(q=0, \omega)\sim|\tau|^{2(\gamma-1)-5\nu}\omega$. Usually[21] $2(\gamma-1)-5\nu\approx2, 7$. We can carry out a similar analysis for systems with long-range action. For uniaxial ferroelectrics we then get

$$\mathrm{Im}\,\tilde{\Lambda}_d(q=0,\omega)\sim|\tau|^{-2}\omega, \tag{4.10}$$

and for intrinsic ferroelastics we get

$$\mathrm{Im}\,\tilde{\Lambda}_d(q=0,\omega)\sim|\tau|^{-3/2}\omega. \tag{4.11}$$

b) *Damping of soft mode*. As already noted in the introduction, the presence of defects in the medium leads to the appearance of local inhomogeneities of the temperature, and consequently to dissipation even in the case of spatially homogeneous changes of $\eta(t)$. We take this circumstance into account in the equations of motion for η and T. In the same approximation as in the preceding subsection, confining ourselves as well for simplicity to the region of applicability of the Landau theory, we have

$$m\ddot{\eta}'+\gamma\dot{\eta}'+\varphi''(\eta_\infty)\eta'-D\nabla^2\eta'+A_0T_c^{-1}\eta_e(\mathbf{r})T'=0, \tag{4.12}$$
$$T\dot{S}=c_\eta\dot{T}'-A_0\eta_e(\mathbf{r})\dot{\eta}'=\varkappa\nabla^2T, \tag{4.13}$$

where $c_\eta=-T(\partial^2\varphi/\partial T^2)_\eta$ is the specific heat at $\tau>0$ far from the transition point, and $\varkappa$ is the thermal-conductivity coefficient. Changing over in the foregoing equations to the Fourier components η' and T' and considering only one component $\eta'(\mathbf{q}, \omega)$, we get

$$(-m\omega^2-i\gamma\omega+\varphi''(\eta_\infty)+Dq^2)\eta'(\mathbf{q},\omega)+A_0T_c^{-1}\sum_{\mathbf{k}}\eta_e(\mathbf{q}-\mathbf{k})T'(\mathbf{k},\omega)=0, \tag{4.14}$$

$$(-i\omega c_\eta+\varkappa k^2)T'(\mathbf{k},\omega)+i\omega A_0\eta_e(\mathbf{k}-\mathbf{q})\eta'(\mathbf{q},\omega)=0. \tag{4.15}$$

Expressing $T'(\mathbf{k}, \omega)$ of (4.15) in terms of $\eta'(\mathbf{k}, \omega)$ and substituting in (4.14), we obtain for the renormalized coefficient $\tilde{\gamma}$ at $\omega=0$ and $q=0$

$$\tilde{\gamma}=\gamma+\frac{A_0^2}{\varkappa T_c}\sum_{\mathbf{k}}\frac{|\eta_e(\mathbf{k})|^2}{k^2}\equiv\gamma+\gamma_d. \tag{4.16}$$

For the contribution of the defects to $\tilde{\gamma}$ we thus obtain

$$\gamma_d\approx\frac{2\pi A_0^2\eta_0^2d^2}{\varkappa T_c}Nr_c^3\sim|\tau|^{-3/2}. \tag{4.17}$$

We compare, as before, γ_d with the contribution of the thermal fluctuations.[43] Confining ourselves only to the first term in formula (3) of Ref. 43, we get

$$\frac{\gamma_d}{\gamma_\Phi}=16\pi^2\frac{\Delta c}{c_\eta}\frac{\Lambda}{\Delta\Lambda}\frac{\Omega^*}{\Omega_T}\left(\frac{\eta_0}{\eta^*}\right)^2\frac{T^*}{T_c}\frac{d}{r_c}Nr_c^3, \tag{4.18}$$

where $\Omega^*\equiv A_0T^*/\gamma T_c$ and $\Omega_T\equiv\varkappa/d^2c_\eta$. At typical values of the parameters, this ratio turns out to be approximately the same as (4.9) in the preceding subsection. Thus, the increase of the damping constant of the soft mode as $\tau\to0$, observed in many experiments,[44] can be due both to thermal fluctuations and to defects.

The considered mechanism of the damping of the soft mode is by far not the only one possible. Thus, for example, oscillations of η lead to oscillations of the crystal deformations. The damping of the deformation oscillations cause in turn energy dissipation, i.e., they cause damping of the oscillations of η. The linear dimensions of the region involved in the oscillations increase as the phase transition point is approached, and this leads to a corresponding increase of the damping coefficient of the soft mode.

5. TEMPERATURE EVOLUTION OF THE STRUCTURE OF THE DEFECT CORE

Everywhere above the value of η_0—of the order parameter at the defect—was assumed given. At the same time, this quantity itself can depend on the temperature. We now take this dependence into account. To this end we regard the free energy of a substance with defects, which is given by (1.1), as a function of η_0 and obtain the equilibrium value η_{0e} from the condition that $\Phi(\eta_0)$ be a minimum. We must first specify the form of the function $f(\eta_0)$, which characterizes the energy of the defect core. The form of this function is determined from symmetry considerations.

We represent $f(\eta_0)$ in the form of a series in powers of η_0, i.e., in the form of an expansion about the point $\eta_0=0$, which usually corresponds to the most symmetrical state of the defect (an example of such a most symmetrical state is shown in Fig. 1c). The function $f(\eta_0)$ must be symmetrical with respect to the transformations that enter in the symmetry group of the crystal with the defect (in the symmetrical phase). If this group contains transformations that alter the sign of η, then the expansion $f(\eta_0)$ contains only even powers of η_0:

$$f(\eta_0)=f_0+\frac{\alpha}{2}\eta_0^2+\frac{\beta}{4}\eta_0^4+\dots, \tag{5.1}$$

In the opposite case the expansion will contain such terms with odd powers of η_0, and the sign of the coefficients at these terms can differ for defects of different localization:

$$f(\eta_0)=f_0\pm|\alpha_1|\eta_0+\frac{\alpha_2}{2}\eta_0^2+\ldots. \tag{5.2}$$

We explain the following using as an example the structural transition in a crystal whose symmetry elements that reverse the sign of η are screw axes. Obviously, these symmetry elements cannot be conserved in the presence of any point defects in an arbitrary site of the crystal, i.e., the symmetry of the crystal + defect system admits of the onset of a nonzero order parameter. In our language this means that $\eta_0\neq 0$. We now subject the crystal + defect system to a screw rotation that enters in the symmetry group of the defect-free crystal. The defect then turns out to be in a different site, and the sign of η_0, and consequently the sign of the coefficients of the odd powers of η_0, is changed. In the case of a multicomponent order parameter there exists, of course, a great variety of types of the function $f(\eta_0)$.

We consider first the temperature dependence of η_0 in the case of defects corresponding to expression (5.2). Minimizing $\Phi(\eta_0)$ and taking (1.11) and (5.2) into account we get

$$\eta_{0e}=\mp\frac{|\alpha_1|}{\alpha_2}\frac{\xi}{1+\xi+d/r_c}+\eta_\infty\frac{1+d/r_c}{1+\xi+d/r_c}, \tag{5.3}$$

where $\xi\equiv\alpha_2 d^2/3D$ is a parameter that characterizes the "rigidity" of the defect core. For very rigid defects ($\xi\to\infty$) the value of η_{0e} is equal to $\mp|\alpha_1|/\alpha_2$ and is independent of τ. Near T_c, the expression for η_{0e} can be written in the form

$$\eta_{0e}=\pm\eta_{00}\left(1-\frac{d/r_c}{1+\xi}\right)+\frac{1}{1+\xi}\eta_\infty, \tag{5.4}$$

where $\eta_{00}\equiv(|\alpha_1|/\alpha_2)\xi/(1+\xi)$ is the value of η_{0e} at the phase-transition point. As follows from (5.4), in the symmetrical phase the absolute value of η_{0e} increases as $\tau\to 0$ in proportion to const $-\tau^{\nu}$. This dependence of η_{0e} should, in particular, be observed in resonance experiments. In the nonsymmetrical phase, the temperature dependence of η_{0e} is determined mainly by the behavior of the last term in formula (5.4) and is different for defects of different polarization. As to the calculation of the contribution of the defect to the above-considered anomalies of the properties of the substance near T_c, allowance for the temperature dependence of η_{0e} does not change qualitatively the results and leads in some cases only to a numerical renormalization of the coefficients.

For the defect to which expression (5.1) corresponds, the values of η_{0e} is determined from the equation

$$\eta_0\left[\alpha+\Delta\alpha\left(1+\frac{d}{r_c}\right)\right]+\beta\eta_0^3=\Delta\alpha\left(1+\frac{d}{r_c}\right)\eta_\infty, \tag{5.5}$$

where $\Delta\alpha\equiv 3D/d^2$. At $\alpha+\Delta\alpha>0$ (we assume the coefficient to be always positive) the equilibrium value of η_0 is zero in the symmetrical phase, while in the nonsymmetrical phase

$$\eta_{0e}\approx\frac{1+d/r_c}{1+\xi+d/r_c}\eta_\infty, \tag{5.6}$$

where, as before, $\xi\equiv\alpha/\Delta\alpha=\alpha d^2/3D$ is the parameter of the "rigidity" of the defect. Such defects contribute to the anomaly only at $T<T_c$. For thermodynamic quantities the character of these anomalies can be determined from formulas (2.2)–(2.4) by putting in them $\eta_0=0$. At $\alpha+\Delta\alpha<0$ the value of η_{0e} is finite at the phase-transition point and is equal to

$$\eta_{0e}=\pm\eta_{00}=\pm\left(-\frac{\alpha+\Delta\alpha}{\beta}\right)^{1/2}. \tag{5.7}$$

The temperature dependence of η_{0e} near T_c is given as before by formulas (5.4) with $\xi=(\alpha+3\beta\eta_{00}^2)d^2/3D$.

As seen from (5.5), at the temperature $T=T_{cd}$, determined from the condition

$$\alpha+\Delta\alpha(1+d/r_c)=0, \tag{5.8}$$

there occurs a unique "phase transition" in the defect, accompanied by the appearance, around the defect, of distortions corresponding to the order parameter. The "phase transition" in the defect was considered in a number of papers[10-14,19] using as concrete examples various systems, and was observed also experimentally.[45,46] Within the framework of our analysis, this transition is of second order, i.e., η_{0e} is a continuous function of the temperature, $\eta_{0e}\sim(T_{cd}-T)^{1/2}$. Of course, a phase transition of first order is also possible in the defect, when the onset of η_{0e} takes place jumpwise. The coefficient β in formula (5.1) is then negative, and terms of sixth order must be taken into account in the expansion of the function $f(\eta_0)$.

Although the quantity T_{cd} can differ substantially from T_c, the "phase transition" in the defect is connected with the phase transition in the matrix, namely, the temperature dependence of the coefficient preceding the first power of η_0 in (5.5) is determined by the temperature dependence of the coefficient A. Naturally, the "phase transition" in the defect could in principle be connected with the temperature dependences of the coefficients α and β irrespective of the temperature dependence of the parameters of the matrix.

We emphasize that the term "phase transition" can be used to describe the restructuring of the defects only figuratively. Actually, this transition affects only a limited number of atoms, and it is well known that in a bounded system the anomalies connected with the phase transition become smoothed out. This smoothing can be taken into account in analogy with the procedure used, for example, in Refs. 47 and 48. In the calculation of the contribution of the defects to the free energy of the system we now use, instead of minimization with respect to η_0, the exact formula

$$\Delta\Phi_d=-k_BT\ln\left\{\int\exp\left[-\Delta\Phi_d(\eta_0)/k_BT\right]d\eta_0\right\}. \tag{5.9}$$

For the temperature width of the smoothing region we then obtain

$$\frac{\Delta T}{T_{cd}}\sim\left(\frac{8}{3\pi}\frac{T_{cd}-T_c}{T_{cd}}\frac{k_BT_c\beta}{dDA_0}\right)^{1/2}. \tag{5.10}$$

It follows from this expression that the quantity $\Delta T/T_{cd}$ can be less than unity actually only in the case when the radius d, of the defect core, greatly exceeds the interatomic distance. Thus, it is hardly possible to discern the restructuring of the core of the defect by means of the thermodynamic anomalies that accompany this restructuring. We note that for defects in a uniaxial ferroelectric or in an intrinsic ferroelastic, the temperature interval over which the smoothing takes place may turn out to be much smaller, since the coefficient of η_0 in (5.5) has, far from T_c, a stronger temperature dependence of the type $C_1 + C_2\tau$.

In the nonsymmetrical phase, as seen from (1.11), states of the defect with different signs of η_0 differ in energy. Far enough from the phase-transition point, at

$$\eta_0 > \frac{2}{3}\frac{|\alpha+\Delta\alpha(1+d/r_c)|^{3/2}}{\Delta\alpha(1+d/r_c)(3\beta)^{1/2}} \qquad (5.11)$$

one of the minima of $\Phi(\eta_0)$ vanishes and all the defects acquire the same sign of η_0. Naturally, the decrease of the number of defects in the metastable state can occur also, without reaching the point where stability of this state is lost, on account of thermal and quantum-mechanical fluctuations. Lowering the temperature below the point of stability loss of the metastable state can serve as a method for obtaining a system of fully polarized defects.

CONCLUDING REMARKS

The theory developed above is phenomenological and in many respects simplified. Its purpose is to describe as many experiments as possible on the basis of expressions that contain only several "microscopic" constants that characterize the core of the defect—its dimension d, its "strength" η_0, and in some cases the rigidity ξ. To compare the theory with experiment it is desirable to carry out a comprehensive set of various measuremets on samples with controlled concentrations of defects of a definite type, and to establish correlations, for example, between the temperature dependence of the specific heat c and the intensity of the scattering of light in these samples. To our knowledge, no such comprehensive investigations have been made so far. It is therefore impossible for the time being to determine the constants of the theory, and to compare it quantitatively with experiment. At the same time, as already illustrated above with a number of examples, the qualitative character of the anomalies introduced by small defect concentrations is apparently correctly described by the theory. Of course, in a detailed comparison with experiment it may be necessary to refine the theory further, for example, by taking into account the anisotropy of the substance, the fact that the order parameter has many components, etc., aside from the interaction of the defects.

In conclusion, we take the opportunity to thank J. Fousek and P. V. Pisarev for acquainting us with their experimental data, S. A. Minyukov for checking individual results, and V. L. Ginzburg and D. E. Khmel'nitskiĭ for useful discussions.

APPENDIX

MODELS OF DEFECTS

We explain, using several examples, the physical meaning of the expressions (5.1) and (5.2) for the energy of the core. Consider a substitutional impurity whose interaction with the matrix is due to one external electron. The total free energy of the system, in the adiabatic approximation, is

$$\Phi = \int \psi^* \hat{H} \psi dV + \int \psi^* \hat{W} \psi dV + \int F(\eta) dV, \qquad (A.1)$$

where $\hat{W}$ is the operator of the interaction of the external electron with the lattice, $\hat{H}$ is the Hamiltonian of the isolated ion, and $F(\eta) \equiv \varphi(\eta) - h\eta + D(\nabla\eta)^2/2$. The usual procedure of determining the state of the defect consists in solving the system of equations for $\psi(\mathbf{r})$ and $\eta(\mathbf{r})$, which are obtained by varying expression (A.1) with respect to these functions.[7] However, for a deep impurity center, for which the dimension of the electron cloud is much smaller than r_c, a different approach is preferable, close to the theory of the crystal field. The operator $\hat{W}$ describes in this case the interaction of the defect only with the matrix atoms that are closest to it, and thus depends on the quantity η_0:

$$\hat{W}(\mathbf{r}) = \hat{W}_0(\mathbf{r}) + \eta_0 \hat{W}_1(\mathbf{r}) + \eta_0^2 \hat{W}_2(\mathbf{r}) + \dots. \qquad (A.2)$$

The operators $\hat{W}_n(\mathbf{r})$ transform in accordance with the irreducible representations of the symmetry group of the defect; this group consists of crystal symmetry elements that do not contain translations. Determining by perturbation theory the contribution made to Φ by the first two terms in (A.1), we get

$$\Phi = g_0\eta_0 + \frac{1}{2}(g_1 - g_2)\eta_0^2 + \dots + \int F(\eta) dV, \qquad (A.3)$$

where

$$g_0 = \int \psi_0^*(\mathbf{r}) \hat{W}_1(\mathbf{r}) \psi_0(\mathbf{r}) dV, \quad g_1 = \int \psi_0^*(\mathbf{r}) \hat{W}_2(\mathbf{r}) \psi_0(\mathbf{r}) dV,$$

$$g_2 = -\sum_m \frac{|\int \psi_0^*(\mathbf{r}) \hat{W}_1(\mathbf{r}) \psi_m(\mathbf{r}) dV|^2}{E_0 - E_m}, \qquad (A.4)$$

in which $\psi_m(\mathbf{r})$ are the wave functions of the states of the "unperturbed" defect. The coefficient g_0 differs from zero in the case when η_0, and consequently also $W_1(\mathbf{r})$, transforms in accordance with the unitary representation of the symmetry group of the defect. Expression (A.2) contains in this case arbitrary powers of η_0 and corresponds to formula (5.2). This situation is realized, for example, in a crystal having as it symmetry elements only screw axes. When η_0 transforms in accordance with a nonunitary representation of the symmetry group of the defect, expression (A.2) contains only even powers of η_0 and corresponds to formula (5.2). We emphasize that the coefficient of η_0^2 in (A.3) can have both signs, inasmuch as $g_2 > 0$ always. We can analogously take into account the dependence of $\hat{W}(\mathbf{r})$ in (A.1) on $(\partial\eta/\partial z)_0$, etc.

We took into account above only the distortion of the electron cloud of the impurity. It is natural to expect, however, that a more important role is played by the displacement of the impurity ion. In this case, the core should be taken to be the impurity ion with its nearest surrounding—the impurity "quasimolecule." The latter is conveniently described by a set of normal coordinates q_i reckoned from that imagined configuration of the quasimolecule in which the quasimolecule in the symmetrical phase does not introduce any distortions corresponding to η. The free energy of the crystal with the defect turns out here to depend on q, η_0, and $\eta(\mathbf{r})$ (Ref. 6). In intrinsic ferroelectrics, where $\eta \equiv P_i$, the quantity q can be identified with the dipole moment of the quasimolecule.[7] For ferroelectric structural phase transitions, q_i can have the meaning of linear combinations of displacements of definite ions of the quasimolecules. In the general case, the physical meaning of the quantities q_i, which characterize the state of the core of the defect, can vary greatly. Thus, for ferromagnets, where $\eta \equiv M$, the quantity q can be identified with the magnetic dipole moment of the core defect. In superconductors, the role of q is played by the magnetic moment of the impurity atom,[14] etc.

One can indicate also cases when the core of the defect has a macroscopic meaning. If the density in the vicinity of the impurity is different than at large distances from the impurity atom, then the coefficients A and B of (1.5) also have different values near the impurity. When the dimension of the region with the smallest density is small, the quantity η hardly changes inside this region, and this region can be regarded as the core of the defect. The change of the density can occur, in particular, because of electrostriction near the charged defect.

For a number of defects, the distortions corresponding to η are quite extended also far from the phase-transition point. Naturally, the influence of such defects cannot be taken into account in the boundary conditions and, strictly speaking, a more detailed analysis is necessary.[12,49,50]

1) This circumstance became clear to us in the course of a discussion with S. A. Minyukov.

2) On the basis of the expression obtained for systems without long-range forces, the experimental data were discussed[8] for an intrinsic ferroelastic transition. For the latter, however, it is necessary to use formula (3.15).

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[1] M. A. Mikulinskiĭ, Usp. Fiz. Nauk **110**, 213 (1973) [Sov. Phys. Usp. **16**, 361 (1973)].

[2] D. E. Khmel'nitskiĭ, Zh. Eksp. Teor. Fiz. **68**, 1960 (1975) [Sov. Phys. JETP **41**, 981 (1975)].

[3] T. C. Lubensky, Phys. Rev. B **11**, 3573 (1975).

[4] Y. Imry and S. Ma, Phys. Rev. Lett. **35**, 1399 (1975).

[5] A. P. Levanyuk and V. V. Osipov, Fiz. Tverd. Tela (Leningrad) **17**, 3595 (1975) [Sov. Phys. Solid State **17**, 2340 (1975)].

[6] A. P. Levanyuk, V. V. Osipov, and A. A. Sobyanin, Theory of Light Scattering in Condensed Matter, Plenum Press, New York, 1976, p. 517.

[7] A. P. Levanyuk, V. V. Osipov, and A. S. Sigov, Ferroelectrics **18**, 147 (1978).

[8] J. D. Axe and G. Shirane, Phys. Rev. B **8**, 1965 (1973).

[9] K. Binder, H. Rauch, and V. Wildpaner, J. Phys. Chem. Solids **34**, 925 (1973).

[10] E. L. Nagaev, Zh. Eksp. Teor. Fiz. **54**, 228 (1968) [Sov. Phys. JETP **27**, 122 (1968)].

[11] H. Suhl, Appl. Phys. **8**, 217 (1975).

[12] B. Ya. Lyubov and V. S. Solov'ev, Fiz. Met. Metalloved. **19**, 333 (1965).

[13] A. F. Andreev, V. I. Marchenko, and A. E. Meierovich, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 40 (1977) [JETP Lett. **26**, 36 (1977)].

[14] L. N. Bulaevskii, V. V. Kusii, and A. A. Sobyanin, Solid State Commun. **25**, 1053 (1978).

[15] N. N. Kristofel', Kristallografiya **18**, 19 (1973) [Sov. Phys. Crystallogr. **18**, 10 (1973)].

[16] M. A. Krivoglaz, Usp. Fiz. Nauk **111**, 617 (1973) [Sov. Phys. Usp. **16**, 856 (1974)].

[17] B. J. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).

[18] S. V. Maleev, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 523 (1977) [JETP Lett. **26**, 383 (1977)].

[19] H. Shmidt and F. Shwabl, Phys. Lett. A **61**, 476 (1977).

[20] K. H. Höck and H. Thomas, Z. Phys. B **27**, 267 (1977).

[21] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), pt. 1, Nauka, 1976., ch. XIV.

[22] A. M. Kosevich, Osnovy mekhaniki kristallicheskoĭ reshetki (Principles of Crystal-Lattice Mechanics), Nauka, 1972, **§ 11.**

[23] A. A. Sobyanin, Zh. Eksp. Teor. Fiz. **61**, 433 (1971) [Sov. Phys. JETP **34**, 229 (1972)].

[24] V. L. Ginzburg and A. A. Sobyanin, Usp. Fiz. Nauk **120**, 153 (1976) [Sov. Phys. Usp. **19**, 773 (1976)].

[25] A. J. Bray and M. A. Moore, J. Phys. A **10**, 1927 (1977).

[26] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionnaya teorya fazovykh perekhodov (Fluctuation Theory of Phase Transitions), Nauka, 1975, ch. II.

[27] A. P. Levanyuk, K. A. Minaeva, and B. A. Strukov, Fiz. Tverd. Tela (Leningrad) **10**, 2443 (1968) [Sov. Phys. Solid State **10**, 1919 (1969)].

[28] A. P. Levanyuk and A. A. Sobyanin, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 540 (1970) [JETP Lett. **11**, 371 (1970)].

[29] L. Bjerkan and K. Fossheim, Solid State Commun. **21**, 1147 (1977).

[30] V. A. Yurin, Izv. Akad. Nauk SSSR Ser. Fiz. **24**, 1329 (1960).

[31] J. B. Hastings, S. M. Shapiro, and B. C. Fraser, Phys. Rev. Lett. **40**, 237 (1978).

[32] A. P. Levanyuk, Fiz. Tverd. Tela (Leningrad) **5**, 1776 (1963) [Sov. Phys. Solid State **5**, 1294 (1964)].

[33] F. P. Jona and G. Shirane, Ferroelectric Crystals, Pergamon 1962 [Mir, 1965, p. 56].

[34] S. A. Taraskin, B. A. Strukov, and V. A. Meleshina, Fiz. Tverd. Tela (Leningrad) **12**, 1386 (1970) [Sov. Phys. Solid State **12**, 1089 (1971)]; R. A. Tobon and J. E. Gordon, Ferroelectrics **17**, 409 (1977).

[35] A. B. Pippard, Philos. Mag. **1**, 473 (1956).

[36] A. P. Levanyuk, Izv. Akad. Nauk SSSR Ser. Fiz. **29**, 879 (1965).

[37] A. I. Larkin and D. E. Khmel'intskiĭ, Zh. Eksp. Teor. Fiz. **56**, 2087 (1969) [Sov. Phys. JETP **29**, 1123 (1969)].

[38] V. L. Ginzburg and A. P. Levanyuk, J. Phys. Chem. Solids **6**, 51 (1958).

[39] G. A. Smolensky, R. V. Pisarev, P. A. Markovin, and B. B. Krichevzov, Physica (Utrecht) **86-88B**, 1205 (1977).

[40] J. Fousek, private communication.

[41] E. F. Steigmeier, H. Auderset, and G. Harbeke, Solid State Commun. **12**, 1077 (1973).

[42] A. P. Levanyuk, Zh. Eksp. Teor. Fiz. **49**, 1304 (1965) [Sov. Phys. JETP **22**, 901 (1966)].

[43] A. P. Levanyuk and N. V. Tsedrina, Fiz. Tverd. Tela (Leningrad) **16**, 1439 (1974) [Sov. Phys. Solid State **16**, 923 (1974)].

[44] P. A. Fleury, Solid State Commun. **8**, 601 (1970); G. Burns and B. A. Scott, Phys. Rev. Lett. **25**, 1678 (1970); S. H. Shapiro and H. Z. Cummins, Phys. Rev. Lett. **21**, 1578 (1968); I. Laulicht, J. Bagno, and G. Shlesinger, J. Phys. Chem. Solids **33**, 319 (1972).

[45] R. Blinc, Ferroelectrics **16**, 33 (1977).

[46] K. A. Müller, N. S. Dala, and W. Berlinger, Phys. Rev. Lett. **36**, 1504 (1976).

[47] V. V. Shmidt, Pis'ma Zh. Eksp. Teor. Fiz. **3**, 141 (1966) [JETP Lett. **3**, 89 (1966)].

[48]A. J. Bray, J. Stat. Phys. 11, 29 (1974).
[49]S. N. Zolotarev, I. B. Sidorova, Yu. A. Skakov, and V. S. Solov'ev, Fiz. Tverd. Tela (Leningrad) 20, 775 (1978) [Sov. Phys. Solid State 20, in press (1979)].
[50]V. M. Nabutovskiǐ and B. Ya. Shapiro, Pis'ma Zh. Eksp. Teor. Fiz. 26, 624 (1977) [JETP Lett. 26, 473 (1977)].

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Mechanism of electron scattering in molybdenum

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The rf size effect was used to study the temperature dependence of the collision frequency $\bar{\nu}(T)$ of electrons and holes in the central sections of various sheets of the Fermi surface of molybdenum. It was found that $\bar{\nu}(T) = \alpha T^2$ at $T \lesssim 9$°K and the value of α was independent of the orbit positions on the octahedral parts of the electron and hole surfaces, and also independent of the purity and thickness of the samples. In the case of small groups (ellipsoids) the range of the quadratic dependence was shifted toward lower temperatures ($T \lesssim 5$°K). Throughout the investigated temperature range (1.2–8°K) the dependence $\bar{\nu}(T)$ for the ellipsoids was well described by a sum of two terms $\bar{\nu}(T) = \alpha T^2 + \beta T^3$. The current concepts were used to calculate the frequency of normal electron–electron collisions in various electron groups, which fitted well the experimental results. An analysis of the data obtained led to the conclusion that the quadratic term in $\bar{\nu}(T)$ of molybdenum was due to the electron–electron scattering.

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Investigations of the temperature dependence of the collision frequency of certain groups of carriers $\bar{\nu}(T)$ on different sheets of the Fermi surface of molybdenum and tungsten have been carried out using the rf size effect method and they have shown that $\bar{\nu}$ rises quadratically with temperature in the liquid helium range.[1] This quadratic law is obtained also in studies of the temperature dependences of the electrical resistivity ρ and thermal resistivity wT of these metals (for a bibliography see Refs. 2 and 3) and it is attributed to the electron–electron scattering. The only argument in support of the electron–electron collisions is the quadratic rise of ρ and wT with temperature. Usually the bulk of electron–electron collisions in transition metals is attributed to the scattering of fast s by heavy d conduction electrons.[2] However, an analysis of the electron structure of molybdenum and tungsten shows that, because of hybridization of the wave functions, the carrier velocities on different sheets of the Fermi surface of these metals differ only slightly[1,4] and, therefore, there is no justification for the use of the $s-d$ scattering theory. This is the main reason why the interpretation of the quadratic law exhibited by molybdenum and tungsten as manifestation of the electron–electron interaction is questioned in Ref. 1. A further study of the temperature dependence of $\bar{\nu}(T)$ for molybdenum was carried out in order to obtain more information on this quadratic dependence. The results, as shown below, provided an experimental proof that the electron–electron collisions are responsible for the quadratic rise of $\bar{\nu}(T)$.

EXPERIMENTS

The rf size effect lines were deduced from the magnetic-field dependences of the first ($\partial R/\partial H$) and second ($\partial^2 R/\partial H^2$) derivatives of the resistive component of the surface impedance of molybdenum samples in the frequency range 3–8 MHz at temperatures 1.2–10°K. The methods used were described in Refs. 1 and 5.

Plane-parallel single-crystal samples of molybdenum were disks ≈6 mm in diameter and with thicknesses d in the range from 0.5 to 2 mm; they were cut by spark machining from ingots whose resistivity ratios were $\rho(293\,^\circ\mathrm{K})/\rho(0\,^\circ\mathrm{K}) \approx 2\times10^4$, 5×10^4, and 10×10^4. Next a layer about 100 μ thick, which was cold-worked in the process of cutting, was removed by grinding with silicon carbide powder of the M-7 grade and subsequent etching in a chemical polishing mixture.[6] The direction of the normal **n** to the surface of the samples was found by x-ray diffraction to within ±0.5° and it coincided with the $\langle 100\rangle$ and $\langle 110\rangle$ axes.

The temperature-dependent part of the collision frequency $\bar{\nu}(T)$ was reduced from the temperature dependence of the amplitude of rf size effect lines $A(T)$, which was described in the $\bar{\nu} > \Omega$ range by the fairly simple expression $A \propto \exp(-\pi\bar{\nu}/\Omega)$ (Ref. 5); here, Ω is the cyclotron frequency and $\bar{\nu} = \bar{\nu}_0 + \bar{\nu}_{ee}(T) + \bar{\nu}_{ep}(T)$ is the sum of the collision frequencies with impurities and defects $\bar{\nu}_0$, with electrons $\bar{\nu}_{ee}(T)$, and with phonons $\bar{\nu}_{ep}(T)$ averaged over a number of points on a selected extremal section of the Fermi surface.[5]

The Fermi surface of molybdenum is well known and consists of an electron "jack," a hole octahedron, six hole ellipsoids, and six electron lenses.[6,7] We investigated the temperature dependences of the electron collisions on various orbits passing along the hole octahedron, the octahedral "waist" of the jack, and ellipsoids. The size effect lines were identified and the experimental results were analyzed as described in Refs. 1, 6, and 7.