Thermodynamics of phase transitions in systems with polarized point defects

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The effect of defects on the properties of substances near second-order phase transitions is analyzed. It is assumed that either the temperatures or the media are such that the Landau theory of phase transitions is applicable. The analysis uses the approach of Levanyuk, Osipov, Sigov, and Sobyanin, [Soviet Phys. JETP **49**, 176 (1979)], in which the substance is described in the continuum approximation, while defects in the substance are taken into account by means of boundary conditions on the continuum equations. These conditions are specified at the core of a defect (the core is the microscopic region around a defect in which the continuum approximation breaks down). A method is proposed within the framework of this approach for reducing the problem of a phase transition in a system with many defects to the problem of a phase transition in separate small volumes, each containing only a single defect. This method is used to completely solve the problem of the properties of a phase transition in a system with point defects in which the sign of the perturbation of the field of the order parameter η caused by these defects is identical for all defects ("polarized" defects). In the case of "strong" defects, which perturb the field of the order parameter both above and below the transition temperature T_c, the effect of the defects essentially reduces to a shift of T_c and the appearance of a mean field h_d, the conjugate of the order parameter, which smears out the phase transition. In the case of "weak" defects, which distort the field of the order parameter only below T_c, the ordering begins at the same temperature, T_{c0} as in the pure crystal. In this case, however, all the thermodynamic quantities have only exponentially weak anomalies at $T = T_{c0}$. Furthermore, in a system with weak defects in random positions the susceptibility diverges in proportion to $\ln h^{-1}$ (h is the external field which is the conjugate of η) in weak fields everywhere below T_{c0}. For systems with polarized point defects, a detailed study is also made of the temperature dependence of the x-ray and neutron scattering intensities and the intensity of light scattering by defects. These quantities are shown to exhibit several clearly defined and distinctive anomalies near the phase transition.

1. INTRODUCTION

The instability of a system at the point of a second-order phase transition (T_c) causes the properties of the system near the phase transition to be anomalously sensitive to various external agents, including defects in the system.[1,2] The actual reason for the very strong effect of defects on the properties of a medium near phasetransitions is that as T approaches T_c the correlation radius of the order parameter increases without bound, and there is an accompanying unbounded increase in the size of the region perturbed by an individual defect. This increase in the size of the perturbed region leads to a strong temperature dependence of the contribution of the defects to various thermodynamic quantities; to an increase in the x-ray, neutron, and light scattering intensities near T_c; to an anomaly in the sound absorption; and to other effects. Even at comparatively low defect concentrations ($n \sim 10^{18}$–10^{19}cm^{-3}) these effects may exceed fluctuational effects by orders of magnitude.[3,4]

The large scale dimension of the spatial distortions of the field of the order parameter near T_c means that these distortions can be described in the approximation of a continuous medium, and the defects in the medium can be taken into account in boundary conditions imposed at the boundary of the defect "core" (that microscopic region near a defect in which the continuum approximation breaks down). A corresponding approach is well known in the case of planar defects (e.g., the surface of a semi-infinite "sample"[5,6]), and it was formulated and developed in Refs. 3 and 4 for the cases of point defects (impurities, vacancies, and interstitial atoms) and line defects (dislocations). The results derived in Refs. 3 and 4, however, apply only to those temperatures and those defect concentrations n such that the average distance between defects is larger than the correlation radius for the order parameter in the pure medium ($nr_c^3 \ll 1$). In this case the solution of the problem is simplified greatly by the circumstance that the perturbations of the order parameter field caused by different defects do not overlap, in practice and the contributions of the individual defects can be calculated independently. We will refer to this approximation as the approximation of "independent" or "noninteracting" defects.

In this paper we wish to go beyond the scope of the approximation of noninteracting defects and to derive for the problem a solution that holds in the entire vicinity of the phase transition. At this stage of the theory, as in Refs. 3 and 4, we restrict the discussion to the simple situation in which a phase transition with a temperature T_{c0} in the pure medium

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is characterized by a single-component order parameter η, and the Landau theory of phase transitions can be used to describe this transition. This means that we are eliminating from consideration the critical (or fluctuational) region, which is extremely small for several substances (e.g., for structural phase transitions in solids[7]) and sometimes is absent altogether.[8]

A second assumption which we will make is that the sign of the perturbations of the field order parameter caused by individual defects is the same for all defects ("polarized" defects). For polarized defects the distribution $\eta(\mathbf{r})$ has no nodes, so that it is the polarized state of the defects which is absolutely stable at $T = 0$. At $T \neq 0$ the defects may in general become disordered. If, however, defect states with opposite signs of the order parameter are separated by a sufficiently high energy barrier ($\Delta \gg k_B T_c$), then even near T_c the polarized state of the defects may persist as a metastable state over extremely long time intervals—significantly longer than typical observation times. These metastable situations are our primary concern here (Sec. 6 discusses practical ways to produce systems with polarized defects).

Yet another important condition which will be used below is that the defect concentration is required to be small in comparison with the concentration of host atoms ($nd^3 \ll 1$, where d is the lattice constant). This is a necessary condition, in particular, for the applicability of the macroscopic phenomenological approach of Ref. 4.

Finally, for brevity we will consider only point defects for which the distribution of the order parameter near the core is spherically symmetric (S-type defects[4]). Polarized point defects of other types and also line defects could be analyzed in an analogous way. As for interacting planar defects, they have already been discussed to some extent in the literature with films of superfluid helium[9] and thin ferromagnetic plates as examples.[10] They have also been discussed in connection with several other questions.[11]

In Sec. 2 of this paper we formulate the problem and the essence of the solution method, which allows us to reduce the problem of a phase transition in a system with many defects to the problem of a phase transition in individual spherical volumes, each centered around only one defect. The problem for one such volume is solved analytically and numerically in Sec. 3. Section 4 deals with the effect of a nonuniformity of the defect distribution (of fluctuations of the defect concentration) on the phase transition through the introduction of a distribution in radius of the number of spherical volumes. In Sec. 5 we calculate the correlation functions which determine the intensity of the elastic scattering of neutrons, x rays, and light by defects in the vicinity of the phase transition. In the concluding remarks in Sec. 6 we discuss certain prospects for the development of this approach and methods for experimentally testing it.

2. FORMULATION OF THE PROBLEM AND THE BASIC IDEA OF THE SOLUTION METHOD

Following Refs. 3 and 4, we write the free energy of a volume V of the substance containing N point defects as

$$\mathscr{F} = \int_{V-\Sigma} [\varphi(\eta) + {}^1/_2 D(\nabla\eta)^2]\,dV + \sum_{i=1}^{N} f(\eta_{0i})\,v_{0i} \tag{1}$$

($\Sigma \equiv \Sigma_i\, v_{0i}$). The first term is the contribution of the host, while the second is the sum of the contributions of the defect cores (which are spherical microscopic regions of radii R_{0i} and volumes $v_{0i} = 4/3\pi R_{0i}^3$ around defects, within which the approximation of a continuous medium breaks down). The energy of the ith core depends on the order parameter η_{0i} at the surface of this core and can be approximated by the following expression for the cases of interest here:

$$\mathscr{F}_{d,\,i} \equiv f(\eta_{0i})\,v_{0i} = 2\pi D\varkappa_i R_{0i}^2 (\eta_{0i} - \eta_{di})^2. \tag{2}$$

The parameters $\varkappa$ and η_d are measures of the "stiffness" and "strength" of the defect, respectively. We will assume below that $\varkappa > 0$ and that the values of $|\eta_{0i} - \eta_{di}|$ are not too large. Otherwise we would have to add to (2) terms of higher order in η_{0i}^2.

For the volume part of the free energy density of the host we use the Landau expansion

$$\varphi(\eta) = \varphi_0 + {}^1/_2 A\eta^2 + {}^1/_4 B\eta^4 - h\eta, \tag{3}$$

where $A = A_0\tau$, $\tau \equiv (T - T_{c0})/T_{c0}$ and h is the field conjugate to η. The distribution of $\eta(\mathbf{r})$ among the defects is then described by the equation

$$D\nabla^2\eta = A\eta + B\eta^3 - h, \tag{4}$$

which is derived by varying (1) with respect to $\eta(\mathbf{r})$.

Expression (2) incorporates as particular cases defects of the type of a "random field h" and defects of the type of a "random local transition temperature." Expression (2) may be thought of as the result of an integration of the following expression over the volume of the system:

$$\int \left\{ \sum_{i=1}^{N} v_{0i} \left({}^1/_2 A_0 \tau_{0i} \eta^2(\mathbf{r})\, \delta(\mathbf{r} - \mathbf{r}_i) - h_{0i}\eta(\mathbf{r})\, \delta(\mathbf{r} - \mathbf{r}_i) \right) \right\} d\mathbf{r} \tag{5}$$

[for brevity we have omitted from (5) terms which do not depend on $\eta(\mathbf{r})$]. The quantities τ_{0i} and h_{0i} are, respectively, the shift of the phase-transition temperature, $T_{ci} = T_{c0}(1 - \tau_{0i})$, and the field h at the position of the defect. They are related to the parameters $\varkappa_i$ and η_{di} by

$$\tau_{0i} = \frac{4\pi D R_{0i}^2 \varkappa_i}{A_0 v_{0i}} = \frac{3D\varkappa_i}{A_0 R_{0i}},$$
$$h_{0i} = \frac{4\pi D R_{0i}^2 \varkappa_i \eta_{di}}{v_{0i}} = \frac{3D\varkappa_i \eta_{di}}{R_{0i}}. \tag{6}$$

It can be seen from (6) that defects of the "random temperature" type correspond to the value $\eta_d = 0$, while defects of the "random field" type correspond to the limit $\varkappa \to 0$, $\eta_d \to \infty$, but $\varkappa\eta_d = R_0 h_0/3D = \text{const}$. It should be kept in mind here that for real defects the parameter $\varkappa$ will not be zero, since a term $\varkappa\eta_0^2$ in the expression for the energy of the defect core is always allowed by the symmetry, so that this limit of random field defects will never be realized in its pure form.

A systematic calculation of the free energy $\mathscr{F}$ of a substance with defects (without thermal fluctuations) would require solving Eq. (4) under the boundary conditions $\eta = \eta_{0i}$ at the surfaces of the defect cores, substituting the resulting solution into (1), and then minimizing (1) with respect to the parameters η_{0i}. In general, this procedure could hardly be implemented without resorting to numerical computer calculations. If the defects are polarized, however, i.e., if the parameter η_d has the same sign for all defects, the solution of the problem can be simplified substantially by taking the following approach.

We assume for simplicity that not only the sign of η_d (which we will assume for definiteness to be positive) but also the magnitudes of the parameters $\varkappa$, R_0, and η_d are the same for all defects. In addition, we initially assume that the defects are "strong": $\eta_d > \eta_e(\tau)$, where η_e is the equilibrium value of the order parameter if there are no defects in the substance. It is then clear that when there are defects in the substance the equilibrium distribution of $\eta(\mathbf{r})$ has maxima at the positions of the defects, while between defects there are minimum surfaces on which we have $(\nabla\eta(\mathbf{r})\cdot\mathbf{n}) = 0$, where $\mathbf{n}$ is the normal to the surface. The corresponding surfaces partition the overall volume of the substance into N small volumes ("cells"), each containing a single defect. Consequently, if the positions of these (extremal) surfaces were known, we could solve Eq. (4) separately in each cell, assuming $(\nabla\eta\cdot\mathbf{n}) = 0$ at the boundary of the cell, and then sum the results over all cells. In practice, the shapes of the various cells may be quite varied, and the problem of finding the positions of the extremal surfaces is equally as difficult as solving Eq. (4) immediately over the entire volume of the crystal. If, however, the defect concentration is small ($nR_0^3 \ll 1$), the particular shape of the individual cells will not be of great importance, and a spherical shape can be used as an approximation. As we will show below (Sec. 3), the function $\eta(\mathbf{r})$ in each cell varies rapidly only in the immediate vicinity of the defect core, while at distances from the defect on the order of several core radii the value of this function can be assumed essentially constant, approximately equal to an average value of η over the cell η ($\bar{\eta} = v^{-1}\int_v \eta(\mathbf{r})\,d\mathbf{r}$). This average value is determined primarily by the cell volume v and depends only slightly on the shape of the cell (the dependence is no stronger than R_0/R, where R is the average cell dimension). For the overwhelming majority of cells with radii $R \gg R_0$, the assumption of spherical cells can thus be assumed justified to an acuracy on the order of the ratio R_0/R. Cells with $R \sim R_0$, in contrast, are encountered statistically rarely; even more importantly, their contribution to the physical quantities varies only slightly with the temperature in the region with $r_c \gg R_0$, i.e., near T_c.

Everything we have said here applies equally well to "weak" defects, with $\eta_d < \eta_e(\tau)$. The only distinction in this case is that there are maxima, rather than minima, in the distribution of $\eta(\mathbf{r})$ among the defects.

Instead of solving Eq. (4) immediately over the entire volume of the system, we partition the system into N spherical volumes and take up the problem of calculating the distribution of $\eta(\mathbf{r})$ and the free energy $\mathscr{F}$ separately in each volume. The next step, as in the case of noninteracting defects, is to sum the results over all volumes, i.e., in the simplest case of uniformly distributed defects to multiply the energy of one such volume, of radius $R = (3/4\pi n)^{1/3}$, by the defect concentration $n = N/V$. The nonuniformity of the defect distribution (i.e., fluctuations of the defect concentration) can be taken into account by introducing the distribution in radius of the number of spherical volumes or, more conveniently, the distribution in the volumes $v = (4/3)\pi R^3$ of the spheres. Specifically, for an uncorrelated, completely random, arrangement of defects, the probability of finding exactly one defect in a given volume of the system is determined by the Poisson formula (see Ref. 12, for example)

$$w_1 = nve^{-nv}, \quad n = N/V.$$

It is then a straightforward matter to derive the following expression for the number of spheres with volumes between v and $v + dv$:

$$dN = f(v)\,dv \equiv Ne^{-nv}d(nv). \tag{7}$$

The function $f(v)$ is obviously the distribution of the number of spheres with respect to volume for an uncorrelated random arrangement of defects.

Using the function f, we can write the average value of the order parameter over the entire volume of the system, or the average value of any other additive physical quantitiy Z, in terms of its average value in a sphere volume v,

$$\bar{Z} = v^{-1}\int_v Z(\mathbf{r})\,d\mathbf{r},$$

as follows:

$$\langle Z\rangle = \frac{N}{V}\int_{v_0}^{\infty} v\bar{Z}(v)e^{-nv}d(vn) = \int_{nv_0}^{\infty} \bar{Z}(x)xe^{-x}dx,$$
$$x = nv. \tag{8}$$

We wish to emphasize that a uniform and essentially random distribution of defects may not be the only case of interest (a Gaussian distribution, for example, may also be of interest). We will restrict the discussion below, however, to only these two limiting cases, in which the distribution funcion of the spheres is a δ-function and when it corresponds to a Poisson distribution.

3. THERMODYNAMIC FUNCTIONS OF SYSTEMS WITH UNIFORMLY DISTRIBUTED DEFECTS

In this case, as we have already state, it is sufficient to solve Eq. (4) in one spherical volume of radius R with the free boundary condition

$$\left.\frac{d\eta}{dr}\right|_{r=R} = 0 \tag{9a}$$

at the surface of this volume and with the condition

$$\eta(r = R_0) = \eta_0 \tag{9b}$$

at the surface of the detect core. We begin with an approximate analytic solution of the problem; we will then compare the results with the results of a numerical integration of Eq. (4). With an eye on further applications, we will not specify the radius R of the volume at the onset; only in the final expressions will we set $R = \bar{R} = (3/4\pi n)^{1/3}$.

We seek an analytic solution of the problem by an iteration method in the parameter $\varkappa_0/\eta_{at}$, where

$$\eta_{at} = (D/BR_0^2)^{1/2} \tag{10}$$

is[4] a characteristic "atomic" value of η, which corresponds, for example, to a complete ordering of the system if we are talking about order-disorder phase transitions. Alternatively, it could correspond to a displacement of sublattices by an amount on the order of the lattice constant if we were dealing with displacement transitions (and so forth).

To take full advantage of this method, we make use of the circumstance that the volume part of the free energy $\int\varphi(\eta)\,dV$ is dominated by the peripheral parts of the volume of the sphere, where $\eta(r)$ is near its extreme value η_m, which is reached at the boundary of the sphere. We thus need to know the distribution $\eta(r)$ and the function $\varphi(\eta)$ as accurately as possible at values of η near η_m. In contrast, the particular function $\varphi(\eta)$ is not very important in finding the distribution $\eta(r)$ near the defect core, since at small values of r the behavior of $\eta(r)$ is detemined primarily by the gradient term in expression (1).

We accordingly expand the function $\varphi(\eta)$ near the point $\eta=\eta_m$ in powers of $\eta-\eta_m$, initially retaining only the first (linear) term (the "linear approximation"):

$$\varphi(\eta)\approx\varphi(\eta_m)+\varphi'(\eta_m)(\eta-\eta_m). \tag{11}$$

We can now replace (1) and (4) by (for a sphere of volume v)

$$\mathscr{F}_v=4\pi\int_{R_0}^{R}\{\varphi(\eta_m)+\varphi'(\eta_m)(\eta-\eta_m)+{}^1/{}_2D[\nabla(\eta-\eta_m)]^2\}r^2dr$$
$$+2\pi DR_0^2\varkappa(\eta_d-\eta_0)^2, \tag{12}$$

$$D\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d(\eta-\eta_m)}{dr}\right)=\varphi'(\eta_m)=\text{const.} \tag{13}$$

A solution of Eq. (13) which satisfies boundary conditions (9) is

$$\eta(r)=\eta_0-\frac{\varphi'(\eta_m)R^3}{3DR_0}\left\{1-\frac{R_0}{r}-\frac{1}{2}\frac{R_0}{R}\left(\frac{r^2}{R^2}-\frac{R_0^2}{R^2}\right)\right\}. \tag{14}$$

Substituting (14) in (12) we find

$$\mathscr{F}_v=[\varphi(\eta_m)+\varphi'(\eta_m)(\eta_0-\eta_m)](v-v_0)-\frac{v^2[\varphi'(\eta_m)]^2G(\rho_0)}{8\pi DR_0}$$
$$+2\pi DR_0^2\varkappa(\eta_0-\eta_d)^2, \tag{15}$$

where

$$G(\rho_0)=(1-\rho_0)^3(1+{}^6/{}_5\rho_0+{}^3/{}_5\rho_0^2+{}^1/{}_5\rho_0^3), \tag{16}$$

and we have defined ρ_0 to be the small ratio R_0/R:

$$\rho_0\equiv R_0/R\ll1. \tag{17}$$

Using (14), we can also easily find the average value of η over the volume $v-v_0$:

$$\bar\eta=\frac{1}{v-v_0}\int_{v-v_0}\eta(\mathbf{r})\,d\mathbf{r}=\eta_0-\frac{\varphi'(\eta_m)R^3G(\rho_0)}{3DR_0(1-\rho_0^3)}. \tag{18}$$

In these expressions, the value of η_m is determined from the self-consistency condition:

$$\eta_m\equiv\eta(r=R)=\eta_0-\frac{\varphi'(\eta_m)R^3}{3DR_0}(1-\rho_0^2)\left(1+\frac{\rho_0}{2}\right). \tag{19}$$

Using (19), we can write $\bar\eta$ as

$$\bar\eta=\eta_m+(\eta_0-\eta_m)\frac{3\rho_0(1+3\rho_0+\rho_0^2)}{10(1+{}^1/{}_2\rho_0)(1+\rho_0+\rho_0^2)}, \tag{20}$$

from which we see that the difference $\bar\eta-\eta_m$ is small by a factor on the order of the parameter ρ_0 in comparison with the total change in the function $\eta(r)$ between the core and the boundary of the sphere. This result confirms that the function $\eta(r)$ is approximately equal to η_m over the greater part of the volume of the sphere, so that it is legitimate to use the sphere model (Sec. 2).

Since the difference $\eta-\eta_m$ is small, we can express the total free energy (15), of the sphere and the self-consistency condition (19) directly in terms of $\bar\eta$. Assuming

$$\varphi(\eta_m)\approx\varphi(\bar\eta)+\varphi'(\bar\eta)(\bar\eta-\eta_m),\quad \varphi'(\eta_m)\approx\varphi'(\bar\eta)$$

and using (20), we find that it is sufficient for this purpose to replace η_m by $\bar\eta$ in expressions (15) and (19). The condition for the validity of this substitution is that the following ratio be small:

$$(\bar\eta-\eta_m)\frac{\varphi''(\bar\eta)}{\varphi'(\bar\eta)}=\frac{\varphi''(\bar\eta)R^2(1-\rho_0^2)(1+3\rho_0+\rho_0^2)}{10D(1+\rho_0+\rho_0^2)}$$
$$\approx{}^1/{}_{10}(R/\bar r_c)^2\ll1, \tag{21}$$

where

$$\bar r_c\equiv[D/\varphi''(\bar\eta)]^{1/2} \tag{22}$$

is the average correlation radius for the order parameter over the volume of the sphere.

A condition analogous to (21) can also be derived by calculating the contribution to $\mathscr{F}_v$ of the quadratic term which we discarded from expansion (11) for the function $\varphi(\eta)$ and by comparing this contribution with that of the linear term. Proceeding in this manner, we find that the range of applicability of the linear approximation is restricted to values of R small in comparison with $\bar r_c$. In other words, this approximation is valid only at temperatures at which the perturbations produced by neighboring defects overlap significantly.

Now minimizing expression (15) with respect to η_0 after first replacing η_m in it by $\bar\eta$, we find

$$\eta_0=\eta_d-\varphi'(\bar\eta)R^3/3D\varkappa R_0^2. \tag{23}$$

For brevity here and in the expressions below [through expressions (30)], we consider only the terms of lowest order in ρ_0. Substituting (23) in (15) and (18) (we again recall that we are replacing η_m by $\bar\eta$ in these expressions), we find

$$F_v\equiv\frac{\mathscr{F}_v}{v}=\varphi(\bar\eta)+\varphi'(\bar\eta)(\eta_d-\bar\eta)-\frac{[\varphi'(\bar\eta)]^2R^3}{6DR_0}\frac{1+\varkappa R_0}{\varkappa R_0}, \tag{24}$$

$$\bar\eta=\eta_d-\frac{\varphi'(\bar\eta)R^3}{3DR_0}\frac{1+\varkappa R_0}{\varkappa R_0}. \tag{25}$$

Expressions (24) and (25) could also be written as

$$F_v=\varphi(\bar\eta)+\frac{b_0}{2}(\eta_d-\bar\eta)^2,\quad b_0=\frac{4\pi DR_0}{v}\frac{\varkappa R_0}{1+\varkappa R_0}, \tag{26}$$

$$\varphi'(\eta)=b_0(\eta_d-\eta), \tag{27}$$

or, if we use the explicit expression for the function φ [expression (3)], in the form

$$F_v=\varphi_0+{}^1/{}_2A_0(\tau+\tau_v)\bar\eta^2+{}^1/{}_4B\bar\eta^4-(h+h_v)\bar\eta, \tag{28}$$

$$A_0(\tau+\tau_v)\bar\eta+B\bar\eta^3-(h+h_v)\bar\eta=0, \tag{29}$$

where

$$\tau_v=\frac{4\pi DR_0}{A_0v}\frac{\varkappa R_0}{1+\varkappa R_0}=\frac{\tau_0}{1+\varkappa R_0}\frac{v_0}{v},$$
$$h_v=\frac{4\pi DR_0}{v}\frac{\varkappa R_0\eta_d}{1+\varkappa R_0}=\frac{h_0}{1+\varkappa R_0}\frac{v_0}{v}. \tag{30}$$

Equations (27) and (29) are actually conditions on the extrema of the free energy density of the sphere, F_v, as a function of $\bar\eta$, and they could be derived by equating the derivative $\partial F_v/\partial\bar{\eta}$ to zero.

Comparing expressions (28) and (3), we see thus that the effect of the defect in the sphere essentially reduces to one of shifting the temperature of the phase transition of the sphere by an amount $\Delta T_c(v) = -T_{c0}\tau_v$ and applying a uniform "external" field h_v on the sphere. Apart from the renormalization factor $K = (1+\varkappa R_0)^{-1}$, these results could easily have been foreseen, since they correspond to simply an average of the local values of τ_0 and h_0 over the total volume of the sphere. On the other hand, the factor K is related to the nonzero stiffness of the defect core, and its appearance could not have been predicted on the basis of dimensional considerations alone.

If we go through the calculations without ignoring the small terms containing the ratio $R_0/R \equiv \rho_0$, we find that the coefficient b_0 in (26) and (27) is replaced by

$$b(\rho_0)=b_0\frac{(1-\rho_0{}^3)(1+\varkappa R_0)}{(1-\rho_0{}^3)^2+\varkappa R_0 G(\rho_0)}, \tag{31}$$

where the function $G(\rho_0)$ is given by (16). The renormalization factor K also depends on ρ_0:

$$K(\rho_0)=\frac{1}{1+\varkappa R_0}\frac{b(\rho_0)}{b_0}.$$

This dependence, however, should not be assigned any great importance, since the approximation of spheres which we have used here is applicable only at small values of ρ_0.

Returning to a system of a large number of uniformly distributed defects, setting $v = 1/n$ in (30), we find the following expressions for the shift of the transition temperature and for the effective field produced by the defects, h_d:

$$\tau_d=\frac{4\pi D\varkappa R_0{}^2 n}{A_0(1+\varkappa R_0)}=\frac{\tau_0}{1+\varkappa R_0}nv_0,$$
$$h_d=\frac{4\pi D\varkappa R_0{}^2 n\eta_d}{1+\varkappa R_0}=\frac{h_0}{1+\varkappa R_0}nv_0. \tag{32}$$

The field h_d smears the phase transition over a typical temperature interval

$$\tau_*=\left(\tau_d\frac{\eta_d}{\eta_{e0}}\right)^{2/3}=\left(\frac{\eta_{at}}{\eta_{e0}}\right)^2\left(\frac{3nv_0\varkappa R_0}{1+\varkappa R_0}\frac{\eta_d}{\eta_{at}}\right)^{2/3}, \tag{33}$$

where $\eta_{e0} = (A_0/B)^{1/2}$ is the equilibrium of the order parameter in a defect-free crystal, extrapolated to $T = 0$. In terms of the reduced variables

$$y=\bar{\eta}/\eta_{e0}\tau_*{}^{1/2},\quad t=(\tau+\tau_d)/\tau_*, \tag{34}$$

we can write Eq. (29) with $h = 0$ in the following "universal" form (a form which does not depend on the parameters of the defects):

$$ty+y^3=1. \tag{35}$$

If $t<t_s = -3\cdot 4^{-1/3}$, this equation has three roots: $y_1>0>y_2>y_3$. The (positive) first root corresponds to a stable state of the polarized system of defects, in which the signs of η_d and $\bar{\eta}$ are the same. The roots y_3 corresponds to a metastable state, in which the sign of η at the defects is opposite the sign of η over the bulk of the host, and the root y_2 determines the height of the barrier between these two states. The temperature T_s thus determines the position of the spinode, above which η_0 state in which η has opposite directions at defects and in the host can occur.

The metastable state which vanishes at $t>T_s$ may complicate the picture of the phase transition in real crystals, since a reorientation of the system of defects or a change in the sign of $\bar{\eta}$ in separate parts of the crystal must be accompanied by the release of latent heat. However, we will restrict the discussion below to only the absolutely stable states, for which the signs of $\bar{\eta}$ and η_d are the same.

The dashed line in Fig. 1a shows the functional dependence $y^2(t)$ for this case, found through the solution of Eq. (35); figures 1b and 1c show (again, the dashed lines) the corresponding temperature dependence of the heat capacity,

$$C_*\equiv\frac{C}{\Delta C}=-\frac{dy^2}{dt}=\frac{2y^2}{3y^2+t}, \tag{36}$$

divided by the jump in the heat capacity $\Delta c = A_0^2/2BT_{c0}$ in an ideal crystal, and the inverse susceptibility

$$\chi_*^{-1}\equiv(A_0\tau_*\chi)^{-1}=\frac{1}{A_0\tau_*}\frac{\partial^2F_v}{\partial\bar{\eta}^2}=3y^2(t)+t, \tag{37}$$

divided by its value $(A_0\tau_*)$ in an ideal system with $\tau=\tau_*$.

This linear approximation holds as long as the condition $R\lesssim\bar{r}_c$ holds [see (21)], as we have already mentioned. To describe the behavior of the thermodynamic functions of the sphere for an arbitrary relation between R and $\bar{r}_c$ and, in particular, to ensure a correct limiting transition to the case of noninteracting defects,[4] we must solve Eq. (4) in the quadratic approximation. By this we mean that we must take into account in expansion (11) for the volume part of the free energy density $\varphi(\eta)$ the term of the next (second) order in the small difference $\eta-\eta_m$:

$$\varphi(\eta)=\varphi(\eta_m)+\varphi'(\eta_m)(\eta-\eta_m)+{}^1/_2\varphi''(\eta_m)(\eta-\eta_m)^2+\ldots.$$

We omit the straightforward but quite lengthy calculations and proceed immediately to the final result: The coefficient b_0 in expressions (26) and (27) is replaced by the function of two variables

$$b(\rho_0,Q)=b_0\frac{1+\varkappa R_0}{\varkappa R_0(1-\rho_0{}^3)}\left[\frac{Q-\operatorname{th}u}{u-(1-\rho_0Q^2)\operatorname{th}u}+\frac{1}{\varkappa R_0}-\frac{3\rho_0}{Q^2(1-\rho_0{}^3)}\right], \tag{38}$$

where $Q\equiv R/\bar{r}_c$, $u=Q(1-\rho_0)$.

For $Q\ll 1$ the function $b(\rho_0,Q)$ is the same as the function $b(\rho_0)$ calculated in the linear approximation [expression (31)], while in the case $Q\gg 1$ this function tends toward a Q-independent value:

$$b(\rho_0,Q)\to b_0\left[1+q\frac{\varkappa R_0}{1+\varkappa R_0+q}\right] \tag{39}$$

($q\equiv R_0/\bar{r}_c$). This value is the same (as it must be) as the value found in Ref. 4 for an isolated defect in an infinite medium. Analysis shows that for arbitrary $\varkappa R_0$ and for all values of the ratio $R_0/\bar{r}_c\equiv q$ the function $\tilde{b}(Q)\equiv b(\rho_0,Q)/b(\rho_0)$ is monotonic and differs from unity by no more than $R_0/\bar{r}_c$. Since we usually have $R_0\sim d$, however, where d is the lattice constant, we see that the ratio $R_0/\bar{r}_c$ is small over essentially the entire range of applicability of our approach, which is based on the approximation of a continuous medium, so that the linear approximation of the function $\varphi(\eta)$ is sufficient for analyzing the behavior of thermodynamic quantities over essentially the entire region of the phase transition.

Let us dwell briefly on the role played by some terms

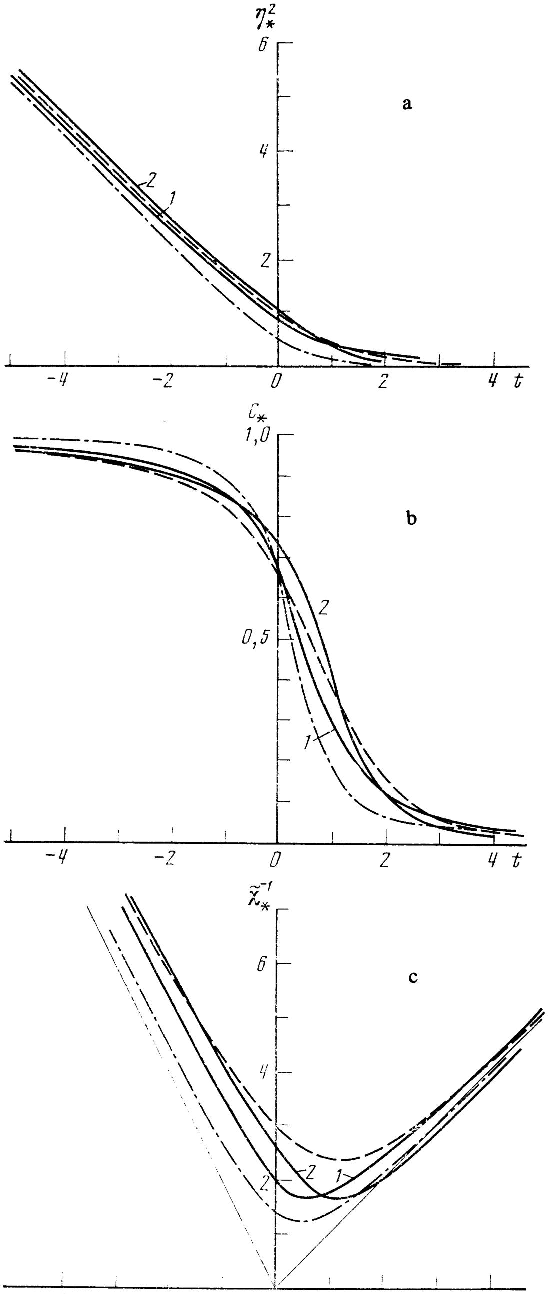

FIG. 1. Temperature dependence of several properties. a: Square of the reduced value of the order parameter, $\eta_*^2(t) \equiv \langle y \rangle^2$. b: Reduced heat capacity ($C_* = \langle C \rangle / \Delta C$). c: Reduced inverse susceptibility ($\chi_*^{-1} = 1/\chi A_0 \tau_*$) in systems with polarized point defects. Dashed lines—uniformly distributed defects; solid lines—randomly distributed defects [1) $s = \infty$; 2) $s = 1$]; dot-dashed lines—results of a numerical integration of Eq. (4) in one spherical volume with a defect for the parameter values $\eta_d/\eta_{at} = 4$, $\varkappa R_0 = 1$, $\rho_0 = 0{,}1$; light lines—common asymptotic behavior of the curves at large $|t|$.

which we have ignored up to this point: the terms of third and fourth order in the expansion of the function $\varphi(\eta)$ in powers of $\eta - \eta_m$ in (11). The contribution of these terms to the free energy of the space can be evaluated most simply by substituting into them the distribution of $\eta(r)$ calculated in the linear approximation or in the quadratic approximation (which is essentially the same as the linear approximation) and by comparing the result found after an integration with the contribution of the gradient term (all three of these terms are essentially zero except in the immediate vicinity of the boundary of the defect core). Going through this procedure, we find that the contribution of these terms is small under the conditions

$$\rho_0 \ln(\rho_0^{-1}) \left(\frac{3\varkappa R_0}{1+\varkappa R_0} \frac{\eta_d}{\eta_{at}} \right)^{4/3} \ll 1, \quad \frac{1}{2} \left(\frac{\varkappa R_0}{1+\varkappa R_0} \frac{\eta_d}{\eta_{at}} \right)^2 \ll 1, \tag{40}$$

or, since $3\varkappa R_0 \eta_d / (1 + \varkappa R_0) \approx \eta_0$ [see (23) and (27)], under the condition $\eta_0/\eta_{at} < 1$.

To find a more precise limitation on the value of the parameter η_0/η_{at}, we also carried out a direct numerical integration of Eq. (4) in a single spherical volume with a defect. We then used the "exact" distributions of $\eta(r)$ to calculate the temperature dependence of $\overline{\eta}$, $\overline{C}$, and $\overline{\chi}^{-1}$. Comparison of this behavior with that found earlier (Fig. 1) shows that the linear approximation yields satisfy results up to $\eta_0/\eta_{at} = 1$. The dot-dashed lines in Fig. 1 show the results of the numerical calculations for one example in the case $\eta_0/\eta_{at} > 1$. We see that even in this case the discrepancies with the dashed lines (the linear approximation) are slight, and at $\eta_0/\eta_{at} < 1$ the results of the numerical calculations essentially conincide with the dashed lines over the entire region of the phase transition.

4. THERMODYNAMIC FUNCTIONS OF SYSTEMS WITH RANDOMLY ARRANGED DEFECTS

If the defects are arranged in a random fashion over the volume of the system, the results derived in the preceding section, for a single sphere of volume v, must be averaged over the ensemble of spheres with the help of Eq. (8). To actually carry out the integration in (8), however, is generally not a simple matter since the quantity $\overline{\eta}(v)$, in terms of which all the other thermodynamic quantities will ultimately be expressed [see (36) and (37), for example], is found through the solution of the cubic equation

$$(t+g/x)\,y+y^3=1/x. \tag{41}$$

Here $x = nv$, and we have transformed to the same dimensionless variables as in (34)–(37). On the other hand, it will be more convenient here to measure the temperature t from the undisplaced transition point ($\tau = 0$), and we denote by g the corresponding relative shift of T_c (expressed in units of the interval over which the phase transition is smeared) which would have occured if the defects had been distributed uniformly in the system:

$$g = \frac{\tau_d}{\tau_*} = \left(3nv_0 \frac{\varkappa R_0}{1+\varkappa R_0} \right)^{1/3} \left(\frac{\eta_{at}}{\eta_d} \right)^{2/3}. \tag{42}$$

Along with g, we will also use the ratio

$$s = \frac{\eta_d}{\eta_s} = g^{-3/2}, \qquad \eta_s = \eta_{at} \left(\frac{3nv_0 \varkappa R_0}{1+\varkappa R_0} \right)^{1/2}, \tag{43}$$

where η_s is a typical value of the force parameter of the defects, η_d, corresponding to $g = 1$.

We will see below that the results are substantially different in the cases $s \ll 1$ (strong defects), $s = 0$ (weak defects), and $s \leqslant 1$ (defects of intermediate strength). We will accordingly discuss these three cases separately.

A. Strong defects ($s \gg 1$)

In the limit $s \to \infty$ ($g = 0$) this case corresponds to "random field" defects. It is easy to show that in this limit the effects of the random distribution of defects play only a minor role. For example, we will calculate the values of $\langle \eta \rangle$, $\langle \chi \rangle$, and $\langle C \rangle$ at $t = 0$, where the effect of the random distribution of defects must be at its greatest for the first two of these quantities. At $t = 0$, Eq. (41) with $g = 0$ has the explicit solution

$$y = x^{-1/3}, \quad t = 0. \tag{44}$$

Substituting this solution into (36) and (37) and then into (8), and integrating over x, we find

$$\eta_* \equiv \langle y \rangle = \langle \eta \rangle / \eta_{e0} \tau_*^{1/2} = \int_0^\infty x^{2/3} e^{-x} dx = \Gamma(5/3) \simeq 0.90\ldots,$$

$$C_* = \langle C \rangle / \Delta C = 2/3,$$

$$\chi_* = \langle \chi \rangle / A_0 \tau_* = 1/3\, \Gamma(8/3) \approx 0{,}5015\ldots. \tag{45}$$

Comparing these values with the corresponding values for uniformly distributed defects [$\eta_* = 1, C_* = 2/3, \chi_* = 1/3$; see (36) and (37)], we see that the discrepancies are slight, reaching 30% only in the case of the susceptibility.

The complete functional depsendences $\eta_*(t)$, $C_*(t)$, and $\chi_*^{-1}(t)$ for defects of this type are shown in Figs. 1a–1c by curves 1 ($s = \infty$) and 2 ($s = 1$). Comparison of these curves with the dashed curves (the uniform case) reveals that at $s \ll 1$ the random distribution of defects does not change the results on the temperature dependence of the thermodynamic quantities in any substantial way from the results for the case of a uniform distribution of defects; this assertion holds not only for $t = 0$ but also throughout the region of the phase transition.

B. Weak defects ($s = 0$).

At $\eta_d = 0$ the energy of a defect core is a quadratic function of the order parameter, and in this sense the case $s = 0$ is the opposite of the discussed above.[1)] This case is also the opposite of the strong-defect case in the sense that the random distribution of defects has a fundamental effect on the nature of the phase transition.

The only scale temperature for weak defects is the quantity τ_d, which determines the average shift of T_c. As units for $\langle \eta \rangle$, $\langle C \rangle$, and $\langle \chi \rangle$ it is convenient to use $\eta_{e0} \tau_d^{1/2}$, ΔC and $(A_0 \tau_d)^{-1}$, respectively. Figure 2 shows the temperature dependence of the thermodynamic quantities normalized in this fashion (we use a tilde to identify them). Since the values of the thermodynamic quantities in the separate spherical volumes v now differ only in the shift of T_c, which is

$$\tau_v = \tau_d / nv = \tau_d / x \tag{46}$$

[see (30) and (31)], it is also a simple matter to calculate these quantities explicitly. For the average value of the order parameter, for example, we have

$$\tilde{\eta} \equiv \frac{\langle \eta \rangle}{\eta_{e0} \tau_d^{1/2}} = \alpha^{-1/2} \int_\alpha^\infty \left(1 - \frac{\alpha}{x}\right)^{1/2} x e^{-x} dx = \frac{\alpha}{2} e^{-\alpha/2} K_1\left(\frac{\alpha}{2}\right), \tag{47}$$

where $\alpha \equiv \tau_d |\tau|$ and K_1 is a modified Bessel function.[13] Using the known asymptotic behavior of this function, we find that in the limit $\alpha \to \infty$ ($|\tau| \to 0$) the order parameter vanishes exponentially,

$$\tilde{\eta} \sim \exp(-\alpha) \sim \exp(-\tau_d / |\tau|), \tag{48}$$

while at $\alpha \ll 1$ ($|\tau| \gg \tau_d$) the dependence $\tilde{\eta}^2(|\tau|/\tau_d)$ approaches a linear dependence

$$\tilde{\eta}^2 = |\tau| / \tau_d - 1, \tag{49}$$

which corresponds to the temperature dependence $\tilde{\eta}_e^2(\tau)$ in the pure substance, but with a shifted transition temperature. The latter result agrees with the result derived in Ref. 4

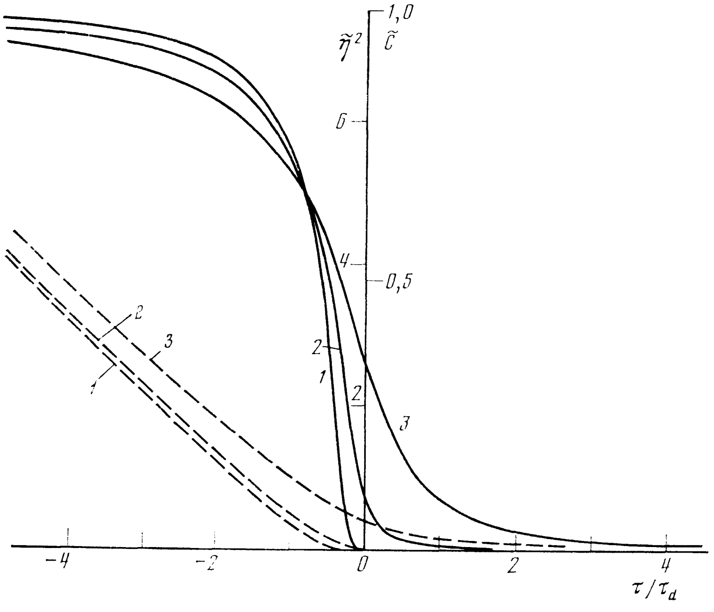

FIG. 2. Temperature dependence of the square of the reduced average order parameter $\langle \eta \rangle^2 / \eta_{e0}^2 \tau_d = \tilde{\eta}^2$ (dashed lines) and of the reduced heat capacity $\tilde{C} = \langle C \rangle / \Delta C$ (solid lines) for systems with weak ($s = 0$) random defects and for systems with defects of intermediate strength s. 1—$s = 0$; 2—$s = 0.2$; 3—$s = 1$.

in the approximation of independent defects.

It is a very simple matter to calculate the heat capacity:

$$\tilde{C}\equiv\langle C\rangle/\Delta C=\int_{\alpha}^{\infty} xe^{-x}dx=(1+\alpha)e^{-\alpha}, \quad \alpha=\tau_d/|\tau|. \tag{50}$$

Under the condition $\alpha \ll 1$ (i.e., far from T_{c0}), the first correction to the heat capacity is proportional to n^2 and thus cannot be calculated in the approximation of independent defects.

It can be seen from (48) and (50) that at the point of the phase transition ($\tau = 0$) the quantities $\langle \eta \rangle$ and $\langle C \rangle$ have only an infinitely weak singularity. We can thus say that in the presence of weak, randomly arranged defects the phase transition converts from second order to infinitely high order.

We turn now to the calculation of the susceptibility. At $\tau \geqslant 0$ we have

$$\tilde{\chi}=A_0\tau_d\langle\chi\rangle=\alpha\int_0^{\infty}\frac{x^2}{\alpha+x}e^{-x}dx=\alpha^3[e^{\alpha}E_1(\alpha)+\alpha^{-2}-\alpha^{-1}], \tag{51}$$

where $\alpha = \tau_d/\tau$, and $E_1(\alpha)$ is the integral exponential function.[13] It follows from (51) that at $\tau = 0$ the susceptibility $\tilde{\chi}$ is finite, equal to 2, while at $\tau \gg \tau_d$ we have

$$\tilde{\chi}^{-1}\approx 1-1/\alpha=\tau/\tau_d+1 \tag{52}$$

in agreement with the approximation of independent defects.[4]

In the region $\tau < 0$ the susceptibility is a diverging function of the external field h for all $|\tau|$:

$$\tilde{\chi}(\alpha)=\tilde{\chi}_1(\alpha)+\tilde{\chi}_2(\alpha)\ln(h_0/h), \quad \alpha=\tau_d/|\tau|, \tag{53}$$

where (see the Appendix)

$$\tilde{\chi}_1(\alpha)=\alpha^3\{[e^{-\alpha}\operatorname{Ei}(\alpha)-\alpha^{-2}-\alpha^{-1}] + e^{-\alpha}({}^3/{}_2\alpha^{-2}+3\alpha^{-1}-3\ln\alpha+c_1)\}, \tag{54a}$$

$$\tilde{\chi}_2(\alpha)=\alpha^3e^{-\alpha}; \tag{54b}$$

$$h_0=0.1(A_0{}^3\tau_d{}^3/B)^{1/2}, \quad c_1\approx 0.87. \tag{54c}$$

The expression in the square brackets in (54a) becomes expression (51) when we replace α in it by $-\alpha$. It follows that without the term which depends logarithmically on h the susceptibility $\tilde{\chi}(\tau)$ is a smooth function which has only an exponentially weak singularity at $\tau = 0$ (curve 1 in Fig. 3). On the other hand, according to (54b) the amplitude of the logaritmically diverging part of χ is approximately zero almost everywhere, except around the point $\tau = -(1/3)\tau_d$, where it has an extremely high and narrow maximum (curve 2 in Fig. 3). Figure 4 shows the temperature dependence of the total susceptibility [see (53)] for various values of h_0/h.

These results can be interpreted as follows. When there is a random arrangement of defects, and there are regions with a relatively high defect concentration, there will obviously also be regions in which there are no defects. The phase transition temperature in the corresponding vacant regions (with a volume $v \gg n^{-1}$) is approximately equal to the critical temperature for the pure substance (T_{c0}), and it is in these regions that a nonzero value of η first arises. Since the numer of large "vacant" regions is exponentially small, however, these regions make only an exponentially small contribution to the thermodynamic quantities. This circumstance also explains why the values of $\langle \eta \rangle$ and $\langle C \rangle$ for systems with randomly arranged weak defects have only an exponentially weak singlularity at $\tau = 0$.

As for the logarithmic divergence of the susceptibility, it stems from the circumstance that for any given temperature $T < T_{c0}$ there are always regions v in which the local value of the critical temperature, $T_c(v) \equiv T_c(n)$ agrees with T and in which the susceptibility has the behavior $\chi(v) \infty |T_c(v) - T|^{-1}$. An integration of this expression over v leads to the logarithmically divergent contribution to the total susceptibility. In a more rigorous theory (which incorporates critical thermal fluctuations), the susceptibility of a bounded volume of the substance must of course remain finite, but we are assuming that the anomalous although bounded increase in the susceptibility in weak fields is retained when critical fluctuations are taken into account.

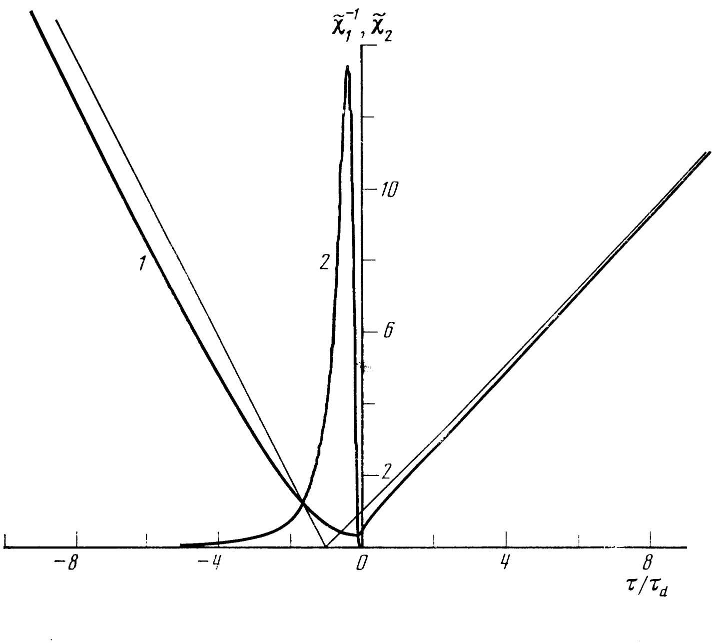

FIG. 3. 1—The function $\tilde{\chi}_1^{-1}(\tau/T_d)$; 2—$\tilde{\chi}_2(\tau/\tau_d)$.

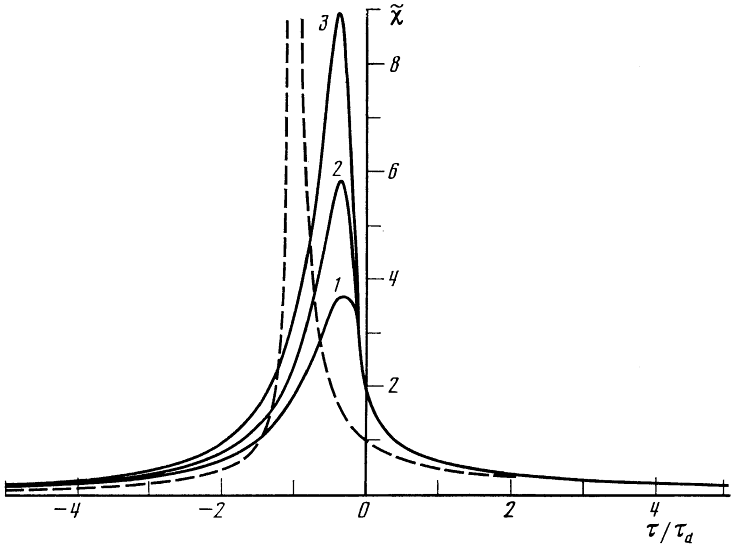

FIG. 4. Temperature dependence of the reduced total susceptibility $\tilde{\chi} = \chi_1 + \tilde{\chi}_2 \ln(h_0/h)$ of a system with weak random defects. 1—$h/h_0 = 0.5$; 2—$h/h_0 = 0.1$; 3—$h/h_0 = 0.01$. The dashed line is the temperature dependence of the susceptibility in a system with a uniform distribution of defects with $h = 0$.

C. Defects of intermediate strength ($s \ll 1$)

The primary distinguishing feature of this case is the existence of a temperature $\tau_1 < 0$ at which the value of the order parameter at a defect core agrees with the equlibrium value in the pure substance: $\eta_d = \eta_e(\tau)$. At $\tau = \tau_1$, the defect evidently does not perturb the order-parameter field, while to the left of this point (at $\tau < \tau_1$) the order parameter decreases, and to the right it increases near the defect core. At $\tau = \tau_1$ we thus have, in a sense, a conversion of the defect from a strong into a weak one.

Let us compare the absolute value of the temperature τ_1 with two other characteristic temperatures: the average shift of the transition temperature, τ_d, and the width of the inteval over which the phase transition is smeared, τ_*. Adopting τ_* as the temperature unit, as in Subsec. 4A, we can write the following simple relationship between the temperatures $t_1 = |\tau_1|/\tau_*$ and $g = \tau_d/\tau_*$:

$$t_1 = g^{-2} = s^{4/3}. \tag{55}$$

If the strength of the defects is low ($s \ll 1$), the temperature t_1 thus lies deep in the interval over which the phase transition is smeared by the effective field of the defects, while at $s > 1$ this temperature lies farther than the other two temperatures from the point $\tau = 0$. In the former case we can expect that the behavior of the thermodynamic quantities will be essentially the same as in the case of weak defects ($s = 0$) throughout the region of the phase transition, while in the latter case, in contrast, the behavior will be similar to that which we saw in Subsec. 4A for random field defects.

The curves $s \neq 0$ in Figs. 1 and 2 confirm these qualitative conclusions. In the region $\tau < \tau_1$ the behavior of the susceptibility for defects with small but nonzero values of s is described well by (53) and (54), after we replace the external field h in them by $h_{\text{eff}} = h_d |\tau|/\tau_d$.

In summary, we can say that the effects of a random arrangement of defects dominate the behavior of the thermodynamic quantities near the phase transition (there is a particularly marked change in the susceptibility) only if the defects are quite weak ($s < 1$). We wish to exphasize that the parameter s depends on the defect concentration [see (43)], so that in practice the transition from the case of strong defects to that of weak defects could in principle be made by varying the defect concentration.

5. INTENSITY OF NEUTRON AND LIGHT SCATTERING BY DEFECTS

The nonuniform distribution of the order parameter in systems with defects is manifest most directly in the scattering of various types of radiation: light, x rays, and neutrons. The corresponding total intensities of this scattering, which is characterized by the scattering wave vector **k**, can be expressed (see Ref. 7, for example), in terms of the spatial Fourier components (with the same vector **k**) of the static correlation function

$$G_1(\mathbf{r}) = \langle [\eta(\mathbf{r}) - \langle\eta\rangle][\eta(0) - \langle\eta\rangle] \rangle$$

in the case of neutron (or x-ray) scattering and the static correlation function

$$G_2(\mathbf{r}) = \langle [\eta^2(\mathbf{r}) - \langle\eta^2\rangle][\eta^2(0) - \langle\eta^2\rangle] \rangle$$

in the case of the scattering of light.[2)]

Here the angle brackets mean (when thermal fluctuations are ignored) an averaging over only the various spatial configurations of the defects, i.e., over the spheres of various radii in our model.

In this section of the paper we discuss the temperature dependence of the zeroth Fourier component of the correlation functions given above. This zeroth component determines the intensity (or cross section) of the small-angle scattering, in which the change in the wave vector upon the scattering is much smaller than the reciprocal of the average distance between defects: $kn^{-1/3} \ll 1$. For this zeroth Fourier component we have

$$I_1(\mathbf{q}=0) \equiv I_1 = \langle \overline{\eta^2} \rangle - \langle \bar{\eta} \rangle^2, \tag{56}$$

$$I_2(\mathbf{q}=0) \equiv I_2 = \langle \overline{\eta^4} \rangle - \langle \overline{\eta^2} \rangle^2, \tag{57}$$

where the superior bar as usual means an average over the volume of the individual spheres. Using the notation $\psi = \eta(\mathbf{r}) - \bar{\eta}$, we can rewrite (56) and (57) as

$$I_1 = [\langle \bar{\eta}^2 \rangle - \langle \bar{\eta} \rangle^2] + \langle \overline{\psi^2} \rangle, \tag{58}$$

$$I_2=[\langle\bar{\eta}^4\rangle-\langle\bar{\eta}^2\rangle^2]+\{\langle\overline{\psi^4}\rangle-\langle\overline{\psi^2}\rangle^2+6\langle\bar{\eta}^2\overline{\psi^2}\rangle$$
$$-2\langle\bar{\eta}^2\rangle\langle\overline{\psi^2}\rangle+4\langle\bar{\eta}\overline{\psi^3}\rangle\}. \qquad (59)$$

These expressions are convenient in that the terms [in (square) brackets] which characterize the effects of the random arrangement of defects are singled out explicitly, as are the terms which are governed primarily by the nonuniformity of the distribution of the parameter η in the individual spherical volumes. For brevity we will refer to that part of an intensity which is determined by the terms in brackets the "fluctuation part," and we will assign it an index "fl." We call the sum of the other terms in expressions (58) and (59) for I_1 and I_2 the "nonuniform part" and assign it an index "non."

We recall that is was shown above that $\bar{\eta}$ for a single sphere can be found in general from the solution of cubic equation (41). We now give expressions for the quantities $\overline{\psi^n}$, which characterize the nonuniformity of the order parameter distribution in a sphere. In calculating the quantities $\overline{\psi^n}$, in contrast with the thermodynamic functions, we cannot in general restrict the analysis to the solution of Eq. (4) in the linear approximation. Nevertheless, the linear approximation does yield good results at $R \ll \bar{r}_c$, while at $R \gg \bar{r}_c$ we can use the expressions from the approximation of noninteracting defects,[4] replacing η_e in them by $\bar{\eta}$. Proceeding in this manner, we find

$$\overline{\psi^2}=\begin{cases}\dfrac{3}{2a}\left(\dfrac{R_0}{R}\right)^2\left[\dfrac{\varkappa R_0}{1+\varkappa R_0}(\eta_d-\bar{\eta})\right]^2, & \dfrac{R}{\bar{r}_c}<a\equiv\dfrac{175}{72}\approx 2.43\\ \dfrac{3}{2}\left(\dfrac{R_0}{R}\right)^3\dfrac{\bar{r}_c}{R_0}\left[\dfrac{\varkappa R_0}{1+\varkappa R_0}(\eta_d-\bar{\eta})\right]^2, & \dfrac{R}{\bar{r}_c}>a\end{cases}, \qquad (60)$$

$$\overline{\psi^3}=\begin{cases}\left(\dfrac{R_0}{R}\right)^3\ln\left(\dfrac{R}{R_0}\right)^3\left[\dfrac{\varkappa R_0}{1+\varkappa R_0}(\eta_d-\bar{\eta})\right]^3, & \dfrac{R}{\bar{r}_c}\lesssim 1\\ \left(\dfrac{R_0}{R}\right)^3\ln\left(\dfrac{\bar{r}_c}{R_0}\right)^3\left[\dfrac{\varkappa R_0}{1+\varkappa R_0}(\eta_d-\bar{\eta})\right]^3, & \dfrac{R}{\bar{r}_c}\gtrsim 1\end{cases}, \qquad (61)$$

$$\overline{\psi^4}=3\left(\frac{R_0}{R}\right)^3\left[\frac{\varkappa R_0}{1+\varkappa R_0}(\eta_d-\bar{\eta})\right]^4 \quad \text{for all} \quad R/\bar{r}_c. \qquad (62)$$

Expressions (60)–(62) differ from the more accurate expressions of the quadratic approximation (which we will not reproduce here because of their length) only at $R\sim\bar{r}_c$. Even in this region, however, the corresponding differences are slight and have essentially no effect on the results.

As in Sec. 4, we will analyze the temperature dependence of the intensities I_1 and I_2 separately for the three cases $s \gg 1$ (strong defects), $s=0$ (weak defects), and $s \ll 1$ (defects of intermediate strength).

A. Strong defects ($s \gg 1$)

In this case the quantity $\bar{\eta}$ is found from the solution of Eq. (41) with $g=0$ (random field defects). Since with $g=0$ no parameters of the defects appear in Eq. (41), we can write the fluctuation parts of the intensities I_1 and I_2 in the following universal form:

$$I_{1\,\text{fl}}=\eta_{e0}^2\tau_* f_1(t), \quad I_{2\,\text{fl}}=\eta_{e0}^4\tau_*^2 f_2(t), \qquad (63)$$

where the functions f_1 and f_2 depend on t alone. Figure 5 shows the functions f_1 and f_2 (normalized to their values at $t=0$). Since Eq. (41) can be solved explicitly in the case $t=0$ [see (44)], the values of the functions f_1 and f_2 at $t=0$ can easily be calculated analytically:

$$f_1(0)={}^1/_3\Gamma({}^1/_3)-{}^4/_9\Gamma^2({}^2/_3)\approx 0.0781,$$
$$f_2(0)=\Gamma({}^2/_3)-{}^1/_9\Gamma^2({}^1/_3)\approx 0.557. \qquad (64)$$

The asymptotic expressions for these functions are

$$f_1(t\gg 1)=t^{-2}[{}^3/_2\ln t-{}^1/_4-\gamma+O(t^{-3/2})], \qquad (65)$$

$$f_2(t\gg 1)=t^{-1}[2-{}^3/_5 t^{-3/2}+O(t^{-2})] \qquad (66)$$

at $t>0$

$$f_1(|t|\gg 1)=(2|t|)^{-2}[{}^3/_2\ln(2|t|)-{}^1/_4-\gamma+O(t^{-3/2})], \qquad (67)$$

$$f_2(|t|\gg 1)=|t|^{-1}[{}^3/_2\ln(2|t|)-\gamma+{}^3/_4+2\sqrt{2}+O(|t|^{-1/2})] \qquad (68)$$

at $t<0$, where γ is Euler's constant.

We wish to draw attention to the distinctive dependence of this type of scattering on the defect concentration. At $|t|\ll 1$, the intensities $I_{1\text{fl}}$ and $I_{2\text{fl}}$ are proportional to $n^{2/3}$ and $n^{4/3}$, respectively, while at $|t|\gg 1$ they are proportional to n^2. For any t this type of scattering is thus fundamentally a many-particle scattering and cannot in principle be described in the approximation of independent defects.[4]

In constrast to the fluctuational parts of the intensities, the nonuniform parts of I_1 and I_2 depend on two, not one, dimensionless parameters. The second dimensonless parameter is the ratio of the correlation radius $\bar{r}_c$ to the average distance between defects or (essentially equivalently) to the average sphere radius $\bar{R}=(3/4\pi n)^{1/3}$. Because of the field h_0 at the position of a defect, the ratio $\bar{r}_c/R$ remains finite even at $t=0$, and at this point it does not depend on the radius of the sphere:

$$\bar{r}_c(0)/R=3^{-1/2}(h_{at}/h_0)^{1/3}.$$

Here h_{at} is a characteristic "atomic" value of the field,

$$h_{at}=B\eta_{at}^3=D^{3/2}B^{1/2}R_0^{-1}, \qquad (69)$$

which causes a change η_{at} in the order parameter in an ideal crystal at $t=0$.

To get an idea of the relative size of the fluctuational and nonuniform contributions, we examine the expressions for the intensities I_1 and I_2 at $t=0$, where they can easily be found explicitly:

$$I_1(0)=\eta_{e0}^2\tau_*\{f_1(0)+p_1(0)(h_0/h_{at})^{4/3}\}, \qquad (70)$$

$$I_2(0)=\eta_{e0}^4\tau_*^2\{f_2(0)+p_{21}(0)(h_0/h_{at})^{4/3}$$
$$+p_{22}(0)(h_0/h_{at})^2-p_{23}(0)(h_0/h_{at})^{8/3}\}. \qquad (71)$$

Here

$$p_1(0)={}^4/_{175}\Gamma({}^1/_3)\approx 0.061, \quad p_{21}(0)$$
$$=a^{-1}[\Gamma({}^2/_3)-{}^1/_9\Gamma^2({}^1/_3)]\approx 0{,}56,$$
$$p_{22}(0)={}^4/_{27}\ln(nv_0)^{-1}\cdot\Gamma({}^2/_3)\approx 0.20\ln(nv_0)^{-1},$$
$$p_{23}(0)=p_1^2(0)\approx 3{,}7\cdot 10^{-3},$$

and the values of $f_1(0)$ and $f_2(0)$ are given above.

Expressions (70) and (71) are valid under the condition $h_0/h_{at}\leqslant a/\sqrt{3}\approx 1{,}4$, and at $h_0/h_{at}>a/\sqrt{3}$ the terms in these expressions containing $(h_0/h_{at})^{4/3}$ and $(h_0/h_{at})^{8/3}$ must be multiplied by $aR/\bar{r}_c=(a/\sqrt{3})(h_0/h_{at})^{1/3}$ and $(a/\sqrt{3})^2(h_0/h_{at})^{2/3}$, respectively [see (60)]. We also note that we have omitted the contribution of the $\langle\psi^4\rangle$ term in (71), since this

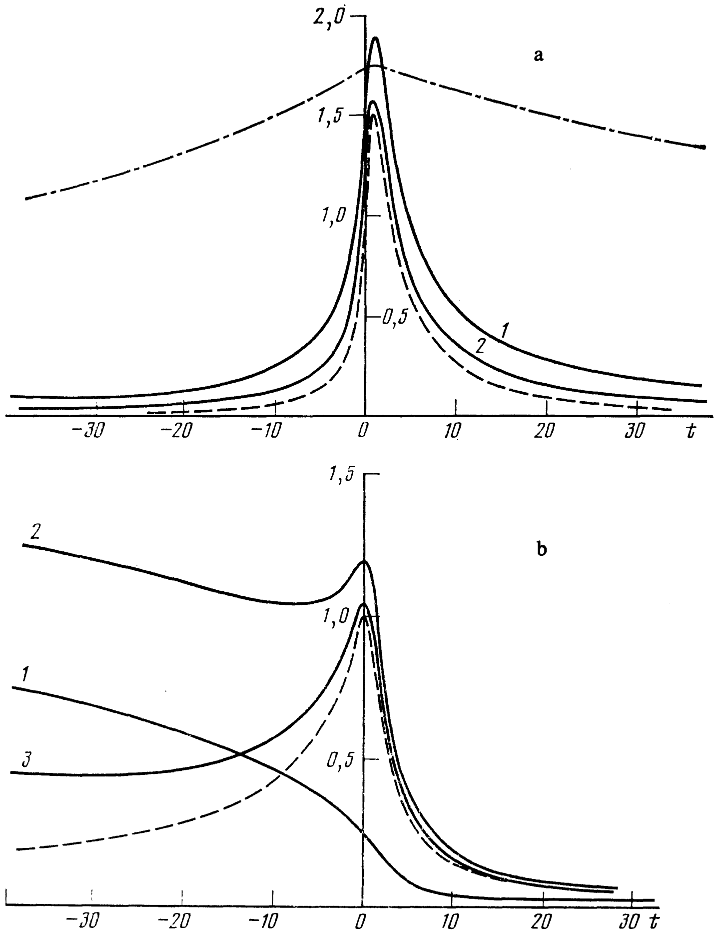

FIG. 5. Temperature dependence of the neutron scattering intensity (a) and the light scattering intensity (b) in systems with "random field" defects. Dashed lines: Fluctuational parts of the intensities (normalized to their values at $t = 0$). Solid lines: Total intensities, normalized in the same way. 1—$h_0/hat = 1$; 2—$h_0/h_{at} = 0.3$; 3—$h_0/h_{at} = 0.1$, where h_{at} is a characteristic "atomic" value of the field; see (69); dot-dashed line—400-fold enlargement of the nonuniform part of the intensity I_1^* for $h_0/h_{at} = 0.03$. Curve 1 in Fig. 5b corresponds to a 10-fold reduction of the intensity $I_2^* = I_2/\eta_{e0}{}^4\tau_*{}^2$.

contribution does not depend on t and can be assigned to a scattering by the defect cores, which is constant near T_c and which we are not considering here.

It can be seen from (70) and (71) that for defects with $h_0 < h_{at}$ the dominant scattering at $t = 0$ is the scattering by fluctuations of the defect concentration, while at $h_0 > h_{at}$ the nonuniform part of the scattering becomes dominant. The random arrangement of defects has only a slight effect on this component of the scattering (not exceeding 10–30%, as in the case of the thermodynamic functions; see Subsec. 4A).

With distance from T_{c0}, the nonuniform part of the scattering falls off more slowly than the fluctuational part, while in the case of the intensity I_2 it in fact increases at $T < T_{c0}$ (because of the increase in $\bar{\eta}$; see the text below and Fig. 5b). At a sufficiently large distance from the transition point, the scattering by nonuniformities, $\eta(r)$, thus becomes dominant even for defects with arbitrarily small values of h_0.

The specific behavior of the intensities $I_{1\text{non}}(t)$ and $I_{2\text{non}}(t)$ can easily be found from (60)–(62), by setting $R = \bar{R} = (3/4\pi n)^{1/3}$ in them (i.e., by ignoring the random arrangement of defects, which, as we have already mentioned, is not very important for the terms with $\overline{\psi^n}$) and by taking the limit $\varkappa \to 0$, $\eta_d \to \infty$, $\varkappa\eta_d = h_0R_0/3D = \text{const}$ (we recall that it is this limit to which defects of the random field type correspond; see (6)]. As a result we find that the temperature dependence of the intensity, $I_{1\text{non}}(t)$, is determined entirely by the ratio $\bar{r}_c/\bar{R}$. In particular, at $\bar{r}_c < \bar{R}$ it falls off in inverse proportion to $\bar{r}_c$ [see (60)]. For defects with $h_0 \ll h_{at}$ the temperature corresponding to $\bar{r}_c = \bar{R}$ is $t_2 \approx (h_{at}/h_0)^{2/3}$ at $t > 0$ for $t_2' \approx -1/2(h_{at}/h_0)^{2/3}$ at $t < 0$. It is approximately at these temperatures that the nonuniform part of the intensity becomes comparable to the fluctuational part.

We thus conclude that for a random arrrangement of random field defects with $h_0 \ll h_{at}$ we should see two maxima, with centers at $t = 0$, on the temperature dependence of the neutron scattering intensity and the intensity of diffuse x-ray scattering. First, there should be a narrow maximum, with a width on the order of the interval over which the phase transition is smeared, τ_*. Second, there should be a broad maximum, with a width on the order of $\tau_*(h_{at}/h_0)^{2/3}$. The height of the narrow maximum will be $\sim(h_{at}/h_0)^{4/3}$ times the height of the broad maximum. With increasing h_0, the second maximum will contrast and increase in height, and it will ultimately merge with the first maximum (Fig. 5a).

For scattering of light (Fig. 5b) the picture is quite different. Here the nonuniform part of the intensity, $I_{2\text{non}}(t)$, increases monotonically with decreasing temperature, because $\bar{\eta}^2(t)$ and $\bar{\eta}(t)$, by which $\overline{\psi^2}$ and $\overline{\psi^3}$ are now multiplied [see (59)], increase more rapidly with distance from T_{c0} than the correlation radius $\bar{r}_c$ decreases. For defects with $h_0 \ll h_{at}$, however, this circumstance does not result in the disapperance of the fluctuational peak, since the nonuniform part of the intensity begins to outweigh the fluctuational part only at a temperature $t_2' = -1/2(h_{at}/h_0)^{2/3}$. As h_0 increases, however, the fluctuational peak becomes progressively less well defined, and at very large values of h_0 ($\gtrsim h_{at}$) it becomes completely masked by the background of the nonuniform part, which is increasing monotonically with the temperature. The asymptotic expressions for $I^*_{2\text{non}} \equiv I_{2\text{non}}/\eta_{e0}{}^4\tau_*{}^2$ at large $|t|$ are

$$I_{2\,\text{non}}{}^*(t \gg t_2) \approx \frac{1}{t}\left[3a\left(\frac{h_0}{h_{at}}\right)^{4/3} + \frac{2}{9}\left(\frac{h_0}{h_{at}}\right)^2 (\ln t)\ln\frac{1}{nv_0}\right], \tag{72}$$

$$I_{2\,\text{non}}(t \ll t_2') = |t|^{1/2}\left[\frac{\sqrt{2}}{3}\frac{h_0}{h_{at}} + \frac{4}{27}\left(\frac{h_0}{h_{at}}\right)^2 (\ln t)\ln\frac{1}{nv_0}\right] + O\left(\frac{1}{|t|}\ln|t|\right). \tag{73}$$

In contrast with the case of neutron scattering, only the second of these asymptotic expressions agrees (in the leading terms) with the expression calculated in the approximation of independent defects.

B. Weak defects ($s = 0$)

A natural scale temperature for the weak defects is the average shift of the transition temperature, τ_d (Subsec. 4B). We will thus understand t in the present subsection to mean the distance from the transition point ($\tau = 0$), expressed in units of τ_d. The fluctuational components of the intensities I_1 and I_2 thus again turn out to be "universal":

$$I_{1\,\text{fl}} = \eta_{e0}{}^2\tau_d \tilde{f}_1(t), \quad I_{2\,\text{fl}} = \eta_{e0}{}^4\tau_d{}^2\tilde{f}_2(t), \tag{74}$$

where

$$\tilde{f}_1 = e^{-\alpha}\alpha^{-1}[1 - {}^1/_4\alpha^2 K_1{}^2(\alpha/2)], \quad \alpha = 1/|t| = \tau_d/|\tau|, \tag{75}$$

$$\tilde{f}_2 = E_1(\alpha) + (\alpha^{-2} - \alpha^{-1})e^{-\alpha} - \alpha^{-2}e^{-2\alpha}. \tag{76}$$

Here we have the asymptotic expressions

$$\tilde{f}_1 \approx |t| \exp(-|t|^{-1}), \quad \tilde{f}_2 \approx 2|t|^3 \exp(-|t|^{-1}) \tag{77}$$

for $|t| \ll 1$ and

$$\tilde{f}_1 \approx \frac{1}{4|t|}[\ln(4|t|) - 0{,}77], \quad \tilde{f}_2 \approx \ln|t| - \gamma - {}^1/_2 \tag{78}$$

for $|t| \gg 1$.

We again call attention to the quadratic dependence of the fluctuational components of the intensities on the defect concentration far from T_{c0}. Figure 6 shows the complete functions $\tilde{f}_1(t)$ and $\tilde{f}_2(t)$. The intensity $I_{1\text{fl}}$ is seen to have a maximum at $t \approx -1$, while the function $I_{2\text{fl}}(t)$ is monotonic, since it is proportional to the higher power $\bar{\eta}^2$.

Again for weak defects, as in the preceding subsection, the nonuniform components of the intensities depend strongly on the ratio $\bar{r}_c/\bar{R}$. In the region with $\bar{r}_c > \bar{R}$ the nonuniform components are significantly smaller than the fluctuational components, while at $\bar{r}_c < \bar{R}$ we have the opposite situation. The temperature t_2 at which we have $\bar{r}_c = \bar{R}$ and at which the nonuniform components become comparable to the fluctuational components in order of magnitude is now determined by the expression

$$|t_2| = |\tau_2|/\tau_d = (nv_0)^{-1/3}(1 + \varkappa R_0)/3\varkappa R_0, \tag{79}$$

from which we see that in the case of low concentrations in which we are interested here we have $|\tau_2| > \tau_d$. At $\tau \ll \tau_2$ the temperature dependence of the nonuniform components is the same as that calculated in the approximation of independent defects:

$$I_{1\,\text{non}} \sim |t|^{1/2}, \quad I_{2\,\text{non}} \sim |t|^2 \ln|t|^{-1}.$$

C. Defects of intermediate strength ($s \lesssim 1$)

The most striking feature in this case is the presence of sharp dips in the intensities, with I_1 and I_2 vanishing at points with a temperature $\tau_1 < 0$, at which we have $\eta_e(\tau_1) = \eta_d$. We recall (See Subsec. 4C) that at $\tau = \tau_1$ the defects convert from "strong" to "weak." At the points τ_1 themselves the defects do not perturb the order parameter field, so that the intensities also vanish.

We should emphasize, however, that in real crystals, because of the unavoidable spread in the values of η_d, this conversion should occur over some temperature interval $\Delta\tau_1$, so that dips will be seen on the $I_1(t)$ and $I_2(t)$ curves (Fig. 6) only when the width $\Delta\tau_1$ of the corresponding region is smaller than the other scale temperatures: the width τ_* of

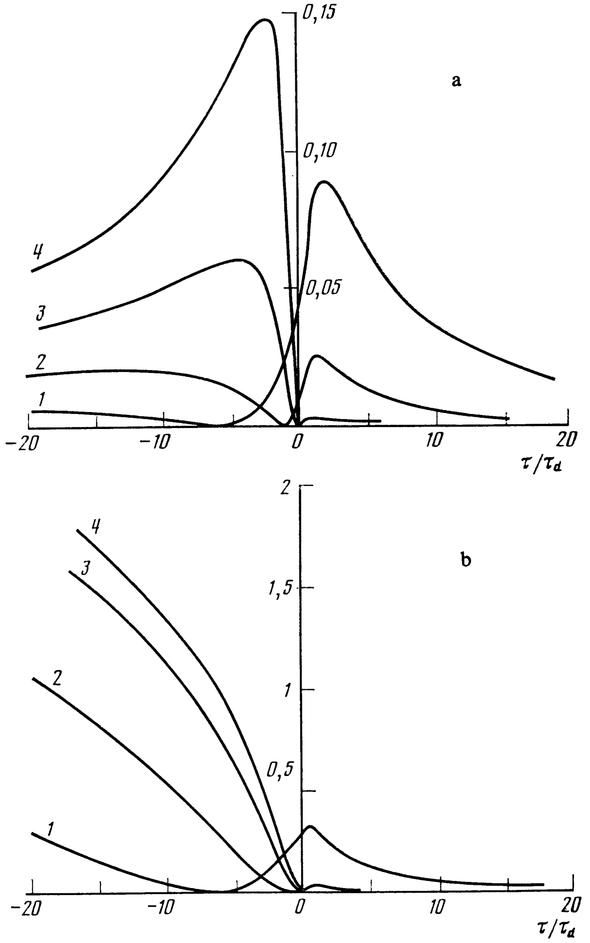

FIG. 6. Temperature dependence of the neutron scattering intensity (a) and of the light scattering intensity (b) in systems with weak defects and with defects of intermediate strength s. 1—$s = 2.5$; 2—$s = 1$; 3—$s = 0.25$; 4—$s = 0$. For simplicity, only the fluctuational components of the intensities I_1 and I_2 (normalized by $\eta_{e0}{}^2\tau_d$ and $\eta_{e0}\tau_d{}^2$, respectively) are shown, since the corresponding nonuniform contributions are small in the region of reduced temperatures under consideration here, $|\tau|/\tau_d \leqslant 20$, and for concentrations $nR_0^3 \leqslant 10^{-4}$.

the interval over which the phase transition is smeared, the shift τ_d of the transition temperature, and, of course, the temperature $|\tau_1|$ itself.

The value of τ_1, i.e., the position of the dip, depends strongly on the parameter s [see (55)]. For example, at $s < 1$ the temperature τ_1 lies closer to the point $\tau = 0$ than do the two other scale temperatures, τ_d and τ_*, while at $s > 1$ we have the opposite relation: $|\tau_1| > \tau_d, \tau_*$. In the calculations it is also important to take into account the position of the temperature (τ_2) at which we have $r_c^3 n = 1$. For the case at hand, with $s \leqslant 1$ and $nv_0 \leqslant 10^4$, the temperature τ_2 lies considerably further from the point $\tau = 0$ than do the other scale temperatures. This circumstance means that we need calculate only the fluctuational components of the intensities over essentially the entire temperature range of interest, since the contribution of the nonuniform parts of the scattering is slight at $|\tau| < |\tau_2|$.

Figure 6 shows some corresponding curves calculated from Eq. (41) and Eqs. (8), (58), and (59). In these figures, τ is expressed in units of τ_d, so that the position of the dips are determined by the value of s^2: $|\tau_1|/\tau_2 = s^2$ [see (55)]. It can be seen from these figures that to the left of the dips the temperature dependence of the intensities approaches that calculated in Subsec. 5B for weak defects ($s = 0$), as expected, while to the right of these points the dependence is approximately that found for strong defects. We repeat that the parameter and thus the nature of the temperature dependence of the intensities could in principle be changed by varying the defect concentration.

In summary, the presence of defects in a system can be seen considerably more clearly and in a greater variety of ways in the anomalous scattering of light, x rays, and neutrons near phase transitions than in the temperature dependence of thermodynamic quantities.[3)]

6. CONCLUDING REMARKS

The approach described above has been based on several assumptions. In particular, we have assumed that the defect concentration is small in comparison with the concentration of the host atoms. Consequently, an experimental test of the results derived above must use extremely pure crystals with an adjustable concentration of an impurity of some species or other. Furthermore, the defects must be "polarized" before the experiments. If the impurity atoms can occupy two stable positions in the crystal cell, corresponding to different signs of η_d, and if these positions are separated by a sufficiently high energy barrier $\Delta > k_B T_c$, then this "polarization" could be implemented in principle by immersing the crystal at some temperature $T > T_c$ in a field h which is the conjugate of the order parameter and then cooling it to a temperature below T_c. If, on the other hand, there is no such field (and this is usually the case for nonferroelectric structural phase transitions), then the crystal may be subjected to other agents which would disrupt the symmetry of the states of the defect with differenct signs of η_d. For example, in quartz cystals one could simultaneously apply a stress in one crystallographic direction and a temperature gradient in another near the point of the $\alpha \leftrightarrows \beta$ structural transition.[14] We might also note that in some cases even the intrinsic ordering effect of the host at low temperatures ($T \ll T_{c0}$) will be sufficient to eliminate the metastable state of the defect with the sign of η_d opposite the sign of the spontaneous value of η in the host.[4] In such cases the single-domain crystal should simply be cooled to the corresponding low temperature and then heated again. To the best of our knowledge, no deliberate experimental effort has been made to produce polarized systems of defects in crystals, although smeared phase transitions are frequently observed experimentally (see Ref. 15, for example).

We wish to emphasize that the difficulty associated with the polarization of defects is not found in systems with weak defects ($\eta_d = 0$), since in this case the defect core has only a single stable state, with $\eta_0 = 0$. The question of methods for producing a system of polarized defects thus actually reduces to the question of methods for producing single-domain "samples."

We turn now to some possiblilities for developing this approach further. We begin with the question of the effect of thermal fluctuations, which we have ignored essentially completely in this paper. Thermal fluctuations play a twofold role. On the one hand, they change the nature of the critical temperature anomalies in the host. On the one other, they have a disorienting effect on the defects. The critical fluctuations (in cases in which they are large) can be taken into account in part by changing the temperature dependence of the coefficients in expansion (3) for the free energy density, as is done in the phenomenological Ψ theory of the superfluidity of helium II near the λ point.[9] A systematic solution of this problem, however, will require the use of the more complicated and subtle methods of the advanced fluctuational theory of critical phenomena.[16]

As for the reorienting effect of fluctuations, we note that in the case in which this reorientation is possible ($\Delta \ll k_B T_c$) we can find a simple estimate of the number of oppositely oriented defects while remaining within the framework of the approach above. For this purpose we need to calculate the difference between the free energies for the states of the defect with different signs of η_d in a sphere of volume v for a given value of $\eta = \eta_m$ at the boundary of the sphere and then compare this difference with the thermal energy. Using (26), we find

$$\frac{\Delta\mathscr{F}_v}{k_B T} \equiv \frac{\mathscr{F}_v^+ - \mathscr{F}_v^-}{k_B T} = \frac{8\pi D R_0^2 \varkappa}{k_B T(1+\varkappa R_0)} \eta_d \bar{\eta}, \tag{80}$$

or, for a sphere of average radius and for $T = T_c = T_{c0}(1 - \tau_d)$ [see (34) and (35)],

$$\frac{\Delta\mathscr{F}_v}{k_B T_c} = \frac{8\pi D R_0 \eta_{at}^2}{k_B T_c} \frac{\varkappa R_0}{1+\varkappa R_0} \frac{\eta_d \eta_{e0} \tau_*^{1/2}}{\eta_{at}^2} = \frac{8\pi}{3} \frac{T_{at}}{T_c} \left[\frac{h_0}{h_{at}(1+\varkappa R_0)}\right]^{4/3} (nv_0)^{1/3}, \tag{81}$$

where $T_{at} \equiv D R_0 \eta_{at}^2 / k_B$ is a atomic temperature (on the order of 10^5 K). The concentration of oppositely oriented defects is $N_- = N \exp(-\Delta\mathscr{F}/k_B T)$, and we see that, with $nv_0 \sim 10^{-3}, T_{at}/T_c \sim 10^3$ and $h_0/h_{at}(1 + \varkappa R_0) \sim 0{,}1$, for example, the defects are polarized all the way to $T - T_c$.

It would of course be interesting to generalize the theory to systems with repolarizing defects ($\Delta\mathscr{F}_v < k_B T_c$) and frozen defects with a random sign of η_d. Just how to make the corresponding generalizations of the theory is not completely clear at this point, but we believe that the idea of initially solving the problem in separate small volumes, rather than immediately over the entire volume of the sytem, should remain useful even in those situations.

Another way to generalize the theory is to examine models of the defect core difference from that used in the present paper. For example, it would be interesting to study the nature of the phase transition in a system with defects whose core energy is[4,17]

$$\mathscr{F}_d=2\pi D R_0^2(\varkappa\eta_0^2+\beta\eta_0^4), \tag{82}$$

where $\varkappa<0$ and $\beta>0$. Here it beomes possible to describe, along with the basic phase transition in the host, the so-called local phase transition[17]: At a certain temperature $T_l > T_{c0}$, the value of the order parameter at the defect cores becomes nonzero. The latter problem is intimately related to that of so-called spin and structural glasses.

Some other important theoretical problems are to take into account the effects of an anisotropy, of long-range forces, and the multicomponent nature of the order parameter.

Clearly, the questions discussed here deserve further study, both theoretical and experimental.

We wish to thank V. L. Ginzburg and L. N. Bulaevskiĭ for a discussion of these results and for several critical comments.

We are also indebted to N. I. Lebedev, A. P. Levanyuk, and A. S. Sigov for the opportunity to see the results of Ref. 18 before its publication.

APPENDIX

We will calculate the susceptibility of a system with a random arrangement of weak defects at $\tau<0$ in two steps. We first find the total average volume $\langle\eta\rangle$, of the order parameter in the presence of a uniform external field h, and we then differentiate $\langle\eta\rangle$ with respect to h.

In the presence of a field h, the average value of η over the volume of a cell is found from the solution of the equation [which follows from (29) with $h_v=0$]

$$A_0|\tau|(\alpha/x-1)\bar{\eta}+B\bar{\eta}^3=h.$$

The change of variables

$$\bar{\eta}=(h/B)^{1/3}y,\quad A_0|\tau|(\alpha/x-1)=h^{2/3}B^{1/3}z$$

puts this equation in the form

$$zy+y^3=1.$$

The solution of the latter equation can be written analytically as follows:

$$y=\begin{cases} z^{-1}-z^{-4}+\ldots, & z>2\\ 1-{}^1/_3z+{}^1/_{81}z^3-\ldots, & -2<z<2.\\ |z|^{1/2}+{}^1/_2|z|^{-1}-{}^3/_8|z|^{-5/2}+\ldots, & z<-2\end{cases}$$

The average $\langle\eta\rangle$ is then determined by the sum of three integrals:

$$\langle\eta\rangle=(h/B)^{1/3}(J_1+J_2+J_3),$$

$$J_1=\int_0^{x_1}[z^{-1}(x)-z^{-4}(x)+\ldots]xe^{-x}\,dx,$$

$$J_2=\int_{x_1}^{x_2}\left[1-\frac{1}{3}z(x)+\frac{1}{81}z^3(x)-\ldots\right]xe^{-x}\,dx,$$

$$J_3=\int_{x_2}^{\infty}\left[|z(x)|^{1/2}+\frac{1}{2}|z(x)|^{-1}-\frac{3}{8}|z(x)|^{-5/2}+\ldots\right]xe^{-x}\,dx,$$

where

$$x_1=\alpha/(1+2\varepsilon),\quad x_2=\alpha/(1-2\varepsilon),$$
$$\varepsilon=h^{2/3}B^{1/3}/A_0|\tau|.$$

Each of these integrals can easily be reduced to a tabulated integral. Differentiating them with respect to h, and retaining only the terms which do not depend on h and which are proportional to $\ln(h^{-1})$, we find the results in (54) for the functions $\tilde{\chi}_1(\alpha)$ and $\tilde{\chi}_2(\alpha)$. The functions $\tilde{\chi}_1$ and $\tilde{\chi}_2$ are determined primarily by only the first term in the integrand for J_1 and by only the first two terms in the integrand for J_3, while all the other terms in J_1 and J_3 and the integral J_2 as a whole affect only the value of the constant c_1 in expression (54a). We calculated the latter quantity approximately, taking into account only the first three terms in each of the integrals.

Note added in proof (30 August 1984). After this paper had been sent to press, we noted that the Fourier transforms of the correlation fuctions $G_1(r)$ and $G_2(r)$ are not the same as the second moments of the distributions $\eta(r)$ and $\eta^2(r)$ but are instead given by the expressions

$$L_1=\frac{V}{n}\int_0^{\infty}x^2(\bar{\eta}-\langle\eta\rangle)e^{-x}\,dx,\qquad L_2=\frac{V}{n}\int_0^{\infty}x^2(\bar{\eta}^2-\langle\eta^2\rangle)e^{-x}\,dx,$$

where (we recall) $x=nv$ and V is the scattering volume. Calculations from these expressions lead to a temperature dependence for L_1n/V and L_2n/V similar to that in Figs. 5 and 6, but there are some differences. Specifically,

a) the scattering occurs only if there is a random arrangement of defects (as should be the case—this is the point that led us to search for an error);

b) the asymptotic expressions for the functions $L_1(\tau)$ and $L_2(\tau)$ as $n\bar{r}_c^2\to 0$ are proportional to n in all cases and are exactly equal to the expressions calculated in the approximation of independent defects [in particular, for weak defects the intensity $L_2(\tau)$ does not increase logarithmically but instead approaches a constant value at $|\tau|\gg\tau_d$];

c) there is only a single maximum in the temperature dependence $L_1(\tau)$ for strong defects, similar to the maximum in the dependence $I_{1\mathrm{fl}}(\tau)$ (Fig. 5), with a height which decreases with increasing defect concentration;

d) the maxima on the curves of $L_1(\tau)$ and $L_2(\tau)$ are more sharply defined than those on the curves of $I_1(\tau)$ and $I_2(\tau)$.

---

[1] In discussing defects with $\eta_d=0$ we are avoiding the phrase "defects of the random temperature type," which is frequently used, since this phrase also applies to defects with $\varkappa<0$, which we are not considering in this paper (see Sec. 6).

[2] An execptional case is that of intrinsic ferroelastic crystals, for which the anomalous part of the light scattering intensity is expressd in terms of the same correlation function as the neutron scattering intensity.[7]

[3)] Analogous problems for a random arrangement of defects with $\eta_d \neq 0$ were solved by Lebedev *et al.*[18,19] They took a completely different approach, based on the solution of linearized equation (4) directly over the entire volume of the systems, followed by an averaging over the coordinates of the individual defects. The linearization was carried out near a fixed (constant over the entire volume) value of the order parameter, $\bar{\eta}$, which was then found from the self-consistency condition $\bar{\eta} = \langle \eta \rangle$. In the model of the present paper, this procedure would correspond to the expansion of the free energy density in each spherical cell [Eq. (11)] around some given value η_m, the same for all cells, which would then be identified with the overall average value of the order parameter in the system ($\eta_m = \langle \eta \rangle$).

We have indeed verified that with this (coincident) choice of origins for the order parameter in each cell our model leads to precisely the same results as those derived in Ref. 18. In the case of a random arrangement of defects, however, which was the only case discussed in Refs. 18 and 19, this method for choosing η_m leads to large and uncontrollable errors for those parts of the system in which the local defect concentration is significantly different from the average value. Consequently, although a local linearization (in the individual cells) of Eq. (4) is completely justified, an immediate localization over the entire volume of the system appears to us to be unjustified. Our results thus naturally do not agree with those derived by Lebedev *et al.*, although for defects with $s \geqslant 1$ (for which the effects of a random distribution are unimportant in several cases) the corresponding differences are more quantitative than qualitative.

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

[2] C. De Dominicis, in: Dynamic Critical Phenomena and Related Topics: Lecture Notes in Physics, Springer-Verlag, Berlin, 1979, p. 251.

[3] A. P. Levanyuk, V. V. Osipov, and A. A. Sobyanin, in: Theory of Light Scattering in Condensed Matter (ed. B. Bendow, J. L. Birman, and V. M. Agranovich), Plenum Press, New York, 1976, p. 517; The Theory of Light Scattering in Solids: Proceedings of the First Soviet American Symposium, Nauka, Moscow, 1976.

[4] A. P. Levanyuk, V. V. Osipov, A. S. Sigov, and A. A. Sobyanin, Zh. Eksp. Teor. Fiz. **76**, 345 (1979) [Sov. Phys. JETP **49**, 176 (1979)].

[5] M. I. Kaganov and A. I. Omelz'yanchuk, Zh. Eksp. Teor. Fiz. **61**, 1679 (1971) [Sov. Phys. JETP **34**, 895 (1972)].

[6] K. Binder, in: Phase Transitions and Critical Phenomena (ed. C. Domb and J. L. Lebowitz), Academic Press, New York, Vol. 10, 1983.

[7] V. L. Ginzburg, A. P. Levanyuk, and A. A. Sobyanin, Usp. Fiz. Nauk **130**, 615 (1980) [*sic!*]; Phys. Rep. **57**, 151 (1980).

[8] A. P. Levanyuk and A. A. Sobyanin, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 540 (1970) [JETP Lett. **11**, 379 (1970)].

[9] V. L. Ginzburg and A. A. Sobyanin, Usp. Fiz. Nauk **120**, 153 (1976) [Sov. Phys. Usp. **19**, 773 (1976)]; J. Low Temp. Phys. **49**, 507 (1982).

[10] M. I. Kaganov and N. S. Karpinskaya, Zh. Eksp. Teor. Fiz. **76**, 2143 (1979) [Sov. Phys. JETP **49**, 1083 (1979)].

[11] H. Schmidt and F. Schwabl, Z. Phys. B **30**, 197 (1978).

[12] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Ch. I, Nauka, Moscow, 1976 (Statistical Physics, Pergamon Press, Oxford (1980).

[13] M. Abramowitz and I. A. Stegun (eds.), Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables, Dover, New York, 1964 (Russ. transl. Nauka, Moscow, 1979).

[14] J. P. Bachheimer and G. Dolino, Phys. Rev. **11** B, 3195 (1975).

[15] G. A. Smolenskiĭ, in: Problemy sovremennoĭ fiziki (Problems of Modern Physics), Nauka, Moscow, 1980.

[16] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Fluktuatsionnaya teoriya fazovykh perekhodov (Fluctuational Theory of Phase Transitions), Nauka, Moscow, 1982.

[17] H. Schmidt and F. Schwabl, Phys. Lett. A **61**, 476 (1977).

[18] N. I. Lebedev, A. P. Levanyuk, and A. S. Sigov, Zh. Eksp. Teor. Fiz. **85**, 1423 (1983) [Sov. Phys. JETP **58**, 825 (1983)].

[19] N. I. Lebedev, A. P. Levanyuk, A. I. Morozov, and A. S. Sigov, Fiz. Tverd. Tela (Leningrad) **25**, 2975, 2979 (1983) [Sov. Phys. Solid State **25**, 1716, 1719 (1983)].

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