SOVIET PHYSICS JETP VOLUME 24, NUMBER 5 MAY, 1967

COLLECTIVE EXCITATIONS NEAR SECOND-ORDER PHASE-TRANSITION POINTS

V. G. VAKS, V. M. GALITSKIĬ, and A. I. LARKIN

Submitted to JETP editor June 22, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 51, 1592—1608 (November, 1966)

It is shown that in systems with a large interaction radius collective excitations with a small and strongly temperature dependent gap in the energy spectrum can exist near points of second-order phase transitions. The self-consistent field method is applied for determining the spectrum of these excitations and the dispersion of the dielectric permittivity in ferroelectric transitions. The anomalies in the excitation spectrum and the dispersion of ϵ near T_C are found to depend on the type and symmetry of the transition. A diagram technique is proposed for calculating successive approximations of the self-consistent field. The technique is used to find the damping of the excitations.

1. INTRODUCTION

IT is commonly accepted that the presence of weakly damped phonons in a solid is connected with the smallness of the anharmonicity of the atomic vibrations near the equilibrium positions. Actually the requirement that the anharmonicity be small is not essential. It is shown in this paper that, for a large interaction radius R_0, weakly-damped excitations can exist in crystals, even though the vibrations of the atoms are not harmonic. The damping of these excitations is inversely proportional to the interaction volume R_0^3 and is small for large R_0. The large radius of interaction insures the applicability of Landau's phenomenological theory of phase transitions.[1] The correctness of this theory for a number of systems in a broad temperature range about T_C is an experimental indication of the possibility of such vibrations.

Unlike in the case of the usual optical phonons, the frequency of these excitations depends on the temperature. The appearance at the phase transition point T_C of spontaneous deformation indicates a decrease in the rigidity of the system with respect to this deformation near T_C. Therefore the frequency of the corresponding vibrations will tend to zero on approaching the transition point. We shall refer to such vibrations as critical. If no phase transition were to occur, then the frequency of these excitations would become imaginary below T_C, which would indicate the instability of the symmetric state.

Ginzburg,[2] Anderson,[3] and Cochran[4] pointed out the possibility of the existence of vibrations with decreasing frequency. However, these studies are phenomenological or qualitative. This paper presents a microscopic treatment of critical excitations. This makes it possible to determine the region of the existence of the vibrations and the physical meaning of the phenomonological parameters. Simple models, unconnected with any specific substance, which include, however, all the essential properties of real crystals are considered. The interaction radius is assumed to be large, which makes it possible to apply the self-consistent field method. The small parameter in the self-consistent field method is the ratio of the volume of a unit cell to the interaction volume $T_C R_0^{-6} \ll |T - T_C| \ll T_C$ where R_0 is the ratio of the interaction radius and the mean distance between the particles. It is shown that the special features in the critical excitation spectrum near T_C are of a different form for triaxial and uniaxial ferroelectrics. The dispersion of the dielectric permittivity is also considered. A diagram technique which makes it possible to calculate further approximations of the self-consistent field method is developed. The damping of the excitations is found with the aid of this method. In the region $|T - T_C| \lesssim R_0^{-6} T_C$ the damping is comparable with the frequency so that the concept of vibrations loses its meaning. The critical vibrations are thus described in the entire region of their existence in the self-consistent field approximation.

2. DESCRIPTION OF THE MODEL. CLASSICAL TREATMENT

In considering the collective vibrations we shall adopt a previously used model.[1] In this model the phase transition consists in the appearance for $T < T_C$ of a mean displacement of a given kind of atom in the unit cell which leads to a reduction of the symmetry. The potential which acts on such an atom in the i-th unit cell consists of a potential produced by atoms of other kinds $U(\mathbf{r}_i)$ and of an interaction with atoms of the same kind in other unit cells—$V_{\mathbf{R}}(\mathbf{r}_i, \mathbf{r}_j)$ where $\mathbf{r}_i$ is the coordinate of the atom in the i-th unit cell relative to the center of the unit cell, and $\mathbf{R} = \mathbf{R}_{ij}$ is the distance between the i-th and j-th unit cell. For the sake of graphic and easy presentation, we assume that the potential $V_{\mathbf{R}}(\mathbf{r}_i, \mathbf{r}_j)$ is of the form $(\mathbf{r}_i \cdot \mathbf{r}_j) V_{\mathbf{R}}$, the potential $U(\mathbf{r})$ is centrally symmetric: $U(\mathbf{r}) = U(-\mathbf{r})$, and the phase transition consists in the appearance of a mean displacement $\langle \mathbf{r} \rangle$ from the center. Let the unit cell, at the center of which the atom is located up to the transition, be tetragonal with a distinguished x axis along which the atom is displaced in the transition. The results will be generalized for the case of arbitrary V and U in Sec. 7.

We shall assume the interaction radius R_0 of the potential $V_{\mathbf{R}}$ to be large compared with the dimensions of the unit cell. This allows one to make use of the self-consistent field method, whose zeroth approximation is equivalent in statistics to the phenomenological theory of second-order Landau phase transitions.[1]

Two very simple types of phase transitions[5] are possible in the model under consideration. In the first of these the potential $U(\mathbf{r})$ has one minimum (Fig. 1a), so that an atom has only a single most probable position in the unit cell. Below the Curie temperature this minimum is shifted by an additional field $\langle \mathbf{r}V \rangle$ due to the displacement of the other atoms. In this case the phase transition is of the "displacement type." In the other case, the potential U has several, for instance two, minima (Fig. 1b). Above the transition, the atom is located with equal probability near each of these minima. Below T_C the field $\langle \mathbf{r}V \rangle$ makes one of these locations more probable. Such a phase transition is an "order-disorder" transition. There are no qualitative differences in the thermodynamic properties of the two types of transitions. However, a difference appears in investigations of vibrations in such systems if the penetrability of the barrier is sufficiently small.

The physical picture of the collective vibrations will be followed in the example of the classical treatment. For simplicity we assume that the potential $U(\mathbf{r})$ can be split into a sum of potentials which depend only on one of the coordinates: $U(\mathbf{r}) = U(r) + U_1(y) + U_2(z)$. Then the motion along different axes is independent and can be considered separately.

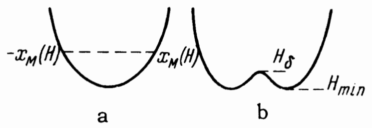

FIG 1

The distribution function of the system $F(x_1, \ldots, x_N, p_1, \ldots, p_N, t)$ is governed by the equation

$$\frac{\partial F}{\partial t} + \sum_i \frac{p_i}{m} \frac{\partial F}{\partial x_i} + \sum_i \left(-\frac{\partial U}{\partial x_i} + \sum_j V_{\mathrm{R}_{ij}} x_j \right) \frac{\partial F}{\partial p_i} = 0. \quad (1)$$

In the zeroth self-consistent field approximation Eq. (1) reduces to the one-particle function f_i, and the interaction with other particles is replaced by an average field determined from the condition of self-consistency:

$$\frac{\partial f_i}{\partial t} + \frac{p}{m} \frac{\partial f_i}{\partial x} + \left(-\frac{\partial U}{\partial x} + E_i \right) \frac{\partial f_i}{\partial p} = 0,$$

$$E_i = \sum_j V_{\mathrm{R}_{ij}} \int x f_j(x, p)\, dx\, dp. \quad (2)$$

In this approximation the function F is split into products of one-particle functions f_i.

The equilibrium function $f_i^{(0)} = f_0(x, p)$ is of the form $f_M(p) n(x)$ where $f_M(p)$ is the Maxwell function, and the density n(x) is given by the equations

$$n(x) = e^{-\beta U(x) + \beta x E_0} \Big/ \int dx\, e^{-\beta U(x) + \beta x E_0},$$

$$E_0 = V_0 s = V_0 \int x n(x)\, dx. \quad (3)$$

Here $\beta = 1/T$, $V_0 = \Sigma_{\mathbf{R}} V_{\mathbf{R}}$ is the zeroth component of the Fourier potential $V_{\mathbf{R}}$, and s is the average displacement.

The phase transition point is determined from (3) as the temperature at which there appears a solution of the equations with $s \neq 0$[1]:

$$T_C = V_0 \overline{x^2}(T_C) = V_0 \int x^2 n(x, T_C)\, dx. \quad (4)$$

The vibrations in the system represent small deviations of the distribution function from its equilibrium form. Therefore we seek the function f_i in (2) in the form

$$f_i(x, p, t) = f_0(x, p) + f(x, p)\, e^{i(\mathbf{k}\mathbf{R}_i - \omega t)}. \quad (5)$$

Here **k** and ω are the wave vector and the excitation frequency. Substituting (5) in (2) and linearizing the equation in f, we obtain

$$i\omega f + \frac{p}{m} \frac{\partial f}{\partial x} + \left(E_0 - \frac{\partial U}{\partial x} \right) \frac{\partial f}{\partial p} = -E_{\mathbf{k}} \frac{\partial f_0}{\partial p};$$

$$E_{\mathbf{k}} = V_{\mathbf{k}} \int x f\, dx\, dp, \qquad V_{\mathbf{k}} = \sum_{\mathrm{R}} V_{\mathbf{R}} \exp(i\mathbf{k}\mathbf{R}). \quad (6)$$

Let us go over in (6) from x and p to new canonical variables H and ξ, where H is the Hamiltonian $p^2/2m + U(x) - xE_0$ and the angle variable ξ[6] defined by the relation $d\xi = dx/v(x, H) = m\,dx/p(x, H)$ denotes the time along the trajectory. x, p, f, and f_0 in (6) are functions of H and ξ, and Eq. (6) takes on the simple form:

$$-i\omega f + \left.\frac{\partial f}{\partial \xi}\right|_H = \frac{\beta E_{\mathbf{k}} f_0(H)}{m} p(\xi, H). \tag{7}$$

The functions $p(\xi)$ and consequently also $f(\xi)$ are periodic with the period T(H). Expanding them in a Fourier series, we obtain

$$f_n = \frac{i\beta E_{\mathbf{k}} f_0(H)}{m(\omega + n\omega_H)}, \quad \omega_H = \frac{2\pi}{T(H)} = \pi\left(\int\limits_{x_{min}}^{x_{max}} \frac{m\,dx}{p(x, H)}\right)^{-1}. \tag{8}$$

The self-consistency condition takes on the form

$$E_{\mathbf{k}} = V_{\mathbf{k}} \int x(\xi, H) f(\xi, H) \frac{d\xi dH}{T(H)} = V_{\mathbf{k}} \sum_n \int dH x_{-n}(H) f_n(H). \tag{9}$$

Substituting (9) in (8) and taking into account the fact that $p_n(H) = -imn\omega_H x_n(H)$, we obtain for the dependence of ω on $\mathbf{k}$ the equation

$$\frac{T}{V_{\mathbf{k}}} - \overline{x^2}(T) = -\int dH f_0(H) x_0^2(H) + 2\omega^2 \times \sum_{n=1}^{\infty} \int dH f_0(H) \frac{|x_n(H)|^2}{n^2\omega_H^2 - \omega^2}, \tag{10}$$

where

$$\overline{x^2} = \sum_n \int dH f_0(H) |x_n(H)|^2 = \int x^2 f_0(x, p)\, dx\, dp.$$

In integrating with respect to H the pole in the right-hand side of Eq. (10) has to be circuited from below; one obtains thus the correct sign of the damping—the imaginary part of ω. However, for the small ω of interest to us the damping obtained from (10) is exponentially small.

For $T = T_C$ and $\mathbf{k} = 0$ the left-hand side of (10) vanishes in accordance with (4). The form of the excitation spectrum depends on the behavior of the function $x_0(H)$ near T_C, i.e., on the value of x averaged over the period which depends on the form of the potential U(x). Above the transition, the average field $E_0 = 0$ and the effective potential $U(x) - x(E_0)$ entering into H coincides with U(x). In the case of potentials with a single minimum (Fig. 1a) the motion occurs in a symmetrical region [from $-x_M(H)$ to $x_M(H)$ on Fig. 1a] and $x_0(H)$ vanishes for all H. In order to simplify the equations, we assume that the interaction V_R is spherically symmetric and has a finite interaction radius R_0 so that its expansion into Fourier components for small k is of the form $V_k = V_0(1 - k^2R_0^2/6)$. Then in the neighborhood of the transition for small $\mathbf{k}$ and ω the spectrum of vibrations is given by

$$a\omega^2 = \frac{1}{6} k^2 R_0^2 + b(T - T_C);$$

$$a = V_0 \left.\frac{\partial \Pi_{\text{c1}}}{\partial \omega^2}\right|_{\substack{T=T_C\\ \omega=0}}, \quad b = -\frac{\partial}{\partial T}(V_0 \Pi_{\text{c1}})\Big|_{\substack{T=T_C\\ \omega=0}},$$

$$\Pi_{\text{c1}} = \beta \sum_n \int dH f_0(H) \frac{|x_n(H)|^2 n^2 \omega_H^2}{n^2\omega_H^2 - \omega^2}. \tag{11}$$

For $T < T_C$ the effective potential $U - xE_0$ is asymmetric, $x_0(H)$ is different from zero, and close to the transition it is proportional to the average displacement $s \sim (T_C - T)^{1/2}$. Utilizing a previously obtained[1] expression for $\overline{x^2}(T)$ below the transition, the dispersion equation for $T < T_C$ can be written in the form

$$a\omega^2 = \frac{1}{6} k^2 R_0^2 + 2b(T_C - T) + \beta V_0 \int dH f_0(H) (x_0(H) - s)^2. \tag{12}$$

Thus for k = 0 the frequency of the "critical" vibrations which are being considered, tends on nearing the transition point to zero like $|T - T_C|^{1/2}$.[2-4]

The situation changes in the case of potentials U(x) with several minima (Fig. 1b). In moving in the region of the left- or right-hand well with an energy H lower than the height of the barrier H_b, the particle does not penetrate into the region of the other well so that the averages over the period of the value of $x_0(H)$ for these H do not vanish. The dispersion equations take on the form

$$a\omega^2 = \frac{k^2R_0^2}{6} + b(T - T_C) + 2\int\limits_{H_{min}}^{H_{\text{б}}} x_0^2(H) f_0(H)\, dH,$$

$$T > T_C,$$

$$a\omega^2 = \frac{k^2R_0^2}{6} + 2b(T_C - T) + \left(\int\limits_{H_{m+}}^{H_b} + \int\limits_{H_{m-}}^{H_b} + \int\limits_{H_b}^{\infty}\right) dH f_0(H)(x_0(H) - s)^2,$$

$$T < T_C, \tag{13}$$

where H_m^+ and H_m^- denote the minima of the right and left well.

For $\mathbf{k} = 0$ and $T \to T_C$ the frequency tends to a finite limit, so that an appreciable decrease in ω will take place only for low barriers: $\beta(H_b - H_{min}) \ll 1$.

Thus, in the classical treatment which we have presented, the presence of an impenetrable barrier which prevents the free displacement of low-energy particles from the left- to the right-hand region leads to an increase in the rigidity of the system to a finite value up to $T = T_C$. In quantum mechanics every barrier has a finite penetrability and, as is shown in the following section, the result that the frequency vanishes turns out (in the self-consistent field approximation) to be correct also for order-disorder transitions.

3. DIELECTRIC PERMITTIVITY. QUANTUM TREATMENT

Above the radius R_0 of interaction between the atoms was considered finite. The results are, for this reason, not directly applicable to the case of ferroelectrics for which the electromagnetic interaction is appreciable. The slow decrease of the electromagnetic forces with distance leads to a number of qualitative effects. To take these into account, one can add to the interaction $V_{\mathbf{R}}$ a term with dipole-dipole interaction.[1] It is, however, more convenient to find the excitation spectrum with the aid of Maxwell's equations, describing the effects of the long-range action by means of an average macroscopic field $\mathbf{E}$[7]:

$$\sum_{\beta=1}^{3}\left[\frac{\omega^2}{c^2}\varepsilon_{\alpha\beta}(\mathbf{k},\omega)-(k^2\delta_{\alpha\beta}-k_\alpha k_\beta)\right]E_\beta = 0. \tag{14}$$

Retardation effects are thereby simultaneously also taken into account.

In the case of tetragonal symmetry under consideration, the non-vanishing components of the dielectric permittivity tensor $\epsilon_{\alpha\beta}$ are $\epsilon_{xx} = \epsilon_{\parallel}$ and $\epsilon_{yy} = \epsilon_{zz} = \epsilon_{\perp}$. The frequency spectrum is determined from the equations

$$\frac{\omega^2}{c^2}\varepsilon_\perp = k^2, \qquad \frac{\omega^2}{c^2}\varepsilon_\parallel\varepsilon_\perp = \varepsilon_\parallel k_\parallel^2 + \varepsilon_\perp k_\perp^2. \tag{15}$$

In the case of cubic symmetry, when $\epsilon_{\parallel} = \epsilon_{\perp}$, the excitation spectrum is independent of the direction of $\mathbf{k}$; in the uniaxial case the spectrum is anisotropic.

The calculation of the dielectric permittivity tensor $\epsilon_{\alpha\beta}(\mathbf{k}, \omega)$ can be carried out by applying the method presented above with the addition to the kinetic equation of a term with an external electric field. We make use of the equation for the density matrix[8] which in the quantum description plays the part of the distribution function. In the self-consistent field approximation this equation is of the form

$$i\frac{\partial\rho_i}{\partial t} = [H_i, \rho_i], \quad H_i = \frac{\hat{p}^2}{2m} + U(\mathbf{r}) - e_{\text{eff}}\,\mathbf{r}_\alpha\left(\mathbf{E}_{i\alpha} + e_{\text{eff}}\sum_{j,\beta} V_{\mathbf{R}_{ij}}^{\alpha\beta}\,\mathrm{Sp}\,x_j{}^\beta\rho_j\right). \tag{16}$$

Here e_{eff} is the effective charge, $\mathbf{E}$ is the average macroscopic field, and $V_{\mathbf{R}}^{\alpha\beta}$ comprises all the short-range forces, including the deviation of the field acting on the atom from the average field. To simplify the equations, we will assume, as above, that the tensor $V_{\mathbf{R}}^{\alpha\beta}$ is equal to $\delta_{\alpha\beta}V_{\mathbf{R}}$ and independent of the coordinates $\mathbf{r}_i$ and $\mathbf{r}_j$, i.e., we neglect the effects of the anisotropy and inhomogeneity of the field within the unit cell. Allowance for these effects is equivalent to considering potentials $V_{\mathbf{R}}(\mathbf{r}_i, \mathbf{r}_j)$ of a general form, and is discussed in Sec. 7. We shall consider the field $\mathbf{E}_i$ to depend periodically on the time and the number of the unit cell: $\mathbf{E}_i = \mathbf{E}\exp i(\mathbf{k}\cdot\mathbf{R}_i - \omega t)$.

In the approximation linear in the field

$$\rho_i = \rho_0 + \rho e^{i(\mathbf{k}\mathbf{R}_i - \omega t)}, \tag{17}$$

where

$$\rho_0 = \frac{e^{-\beta H_0}}{\mathrm{Sp}\,e^{-\beta H_0}}, \qquad H_0 = \frac{p^2}{2m} + U(\mathbf{r}) - xV_0 s, \qquad s = \mathrm{Sp}\,x\rho_0. \tag{18}$$

The equation for ρ is obtained by linearizing (16):

$$\omega\rho = [H_0, \rho] + \sum_\alpha [x^\alpha, \rho_0](E_\alpha + V_{\mathbf{k}}\,\mathrm{Sp}\,x^\alpha\rho). \tag{19}$$

This equation is conveniently solved in terms of the representation of the eigenfunctions $\psi_\nu(\mathbf{r})$ of the operator H_0 which satisfy the equation $H_0\psi_\nu = \epsilon_\nu\psi_\nu$. As a result, we obtain for the dielectric permittivity $\epsilon_{\alpha\beta}$ defined by the equation

$$\sum_\beta \varepsilon_{\alpha\beta}E_\beta = E_\alpha + \frac{4\pi e_{\text{eff}}^2}{v_{\text{я}}}\,\mathrm{Sp}\,x^\alpha\rho, \tag{20}$$

where v_{un} is the volume of a unit cell,

$$\varepsilon_\parallel(\mathbf{k},\omega) = 1 + \frac{\lambda\Pi_\parallel(\omega)}{1 - V_{\mathbf{k}}\Pi_\parallel(\omega)},$$

$$\varepsilon_\perp(\mathbf{k},\omega) = 1 + \frac{\lambda\Pi_\perp(\omega)}{1 - V_{\mathbf{k}}\Pi_\perp(\omega)}. \tag{21}$$

Here

$$\lambda = \frac{4\pi e_{\text{eff}}^2}{v_{\text{я}}}, \qquad \Pi_{\alpha\beta}(\omega, T) = \sum_{\mu,\nu} x_{\mu\nu}{}^\alpha x_{\nu\mu}{}^\beta\frac{n_\mu - n_\nu}{\omega_{\nu\mu} + \omega},$$

$$\omega_{\nu\mu} = \varepsilon_\nu - \varepsilon_\mu,$$

$$n_\mu = e^{-\beta\varepsilon_\mu}/\mathrm{Sp}\,e^{-\beta H} = e^{-\beta\varepsilon_\mu}\Big/\sum_\nu e^{-\beta\varepsilon_\nu}. \tag{22}$$

$$1 = V_0 \sum_{\mu,\nu} |x_{\mu\nu}|^2 \frac{n_\nu(T_C) - n_\mu(T_C)}{\omega_{\mu\nu}} \Bigg|_{s=0} = V_0 \Pi_{\parallel}(0, T_C). \tag{23}$$

In order to find the behavior of $\epsilon_{\alpha\beta}$ close to the transition, we compare (21) with the equation for finding the Curie temperature T_C which is defined as the point at which a non-zero displacement s appears. Assuming that in the last equation of (18) $s \rightarrow 0$, we find that T_C satisfies the equation

Substituting (23) in (21), we find that close to the transition for frequencies small compared with the optical frequencies, $\sim \omega_{\mu\nu}$, and wavelengths that are large compared with the interaction radius R_0 of the potential V_R, the dielectric permittivity $\epsilon_{\parallel}$ is of the form

$$\varepsilon_{\parallel}^{\pm}(\mathbf{k}, \omega) = 1 + \frac{1}{k^2\delta + |T - T_C| a_{\pm} - \omega^2/\omega_0^2}. \tag{24}$$

The signs ± denote here the regions above and below T_C, and we have introduced the notation

$$\delta = \frac{R_0^2}{6}\frac{V_0}{\lambda}, \qquad a_+ = -\frac{V_0^2}{\lambda}\frac{\partial \Pi_{\parallel}}{\partial T}\Bigg|_{\substack{T=T_C \\ \omega=0}}$$

$$= -\frac{V_0^2}{\lambda}\frac{d}{dT}\sum_{\mu\neq\nu}\frac{n_\mu - n_\nu}{\omega_{\mu\nu}} x_{\mu\nu}^2\Bigg|_{T_C}$$

$$a_- = 2a_+ + \frac{V_0 \sum_\nu n_\nu (x_{\nu\nu} - s)^2}{T_C(T_C - T)},$$

$$\omega_0^{-2} = \frac{V_0^2}{\lambda}\frac{\partial \Pi_{\parallel}}{\partial \omega^2}\Bigg|_{\substack{T=T_C \\ \omega=0}}. \tag{25}$$

The quantity δ in (24) and (25) coincides with the coefficient of the gradient term in the free energy, introduced in the phenomenological description of inhomogeneity effects.[9] The constant a_+^{-1} coincides with the static value of the Curie-Weiss constant; the constant a_- is, as in the classical formula (12), larger than the corresponding static value $2a_+$. This difference, connected with the neglect of relaxation processes, is discussed in Sec. 5. It is seen from (24) that near the transition $\epsilon_{\parallel}$ is large for small **k** and ω. In a phase transition from a cubic to a tetragonal unit cell, the permittivity $\epsilon_{\perp}$ is also singular near the transition; it is then of the form

$$\varepsilon_{\perp} = 1 + \frac{1}{k^2\delta + |T - T_C| b_{\pm} - \omega^2/\omega_0^2}$$

where $b_+ = a_+$, and b_-^{-1} is the static value of the Curie-Weiss constant for the transverse permittivity below T_C.[7]

4. EXCITATION SPECTRUM

Substituting $\epsilon_{\alpha\beta}(\mathbf{k}, \omega)$ in Eq. (15), one can find the excitation spectrum.

Let us first consider the simplest case when the crystal is cubic above the transition. In this case, $\epsilon_{\perp} = \epsilon_{\parallel} = \epsilon$ in Eqs. (15), and the spectrum is independent of the direction of **k**. One branch of excitations corresponds to longitudinal vibrations whose spectrum is given by the equation $\epsilon(\mathbf{k}, \omega) = 0$. Making use of (24), we find that for small k and $T - T_C$ the frequency of these vibrations is ω_0. If the ratio λ/V_0 is not small, then these excitations lie outside the region of applicability of the approximation $\omega \ll \omega_{\nu\mu}$ which we have used. The two transverse vibrations have an identical frequency, given by the first of Eqs. (15):

$$\omega^2 = \frac{a_+(T - T_C) + k^2\delta}{\omega_0^{-2} + (ck)^{-2}}. \tag{26}$$

The spectrum of these excitations is shown in Fig. 2.

For very small k the excitation is an electromagnetic wave propagating with a velocity determined by the static ϵ. For $k \gg \omega_0/c \sim 10^2$–$10^3$ cm^{-1} the spectrum has the form of optical vibrations with a gap which vanishes at the transition point:

$$\omega^2 = \omega_0^2[a_+(T - T_C) + k^2\delta]. \tag{27}$$

Below T_C the crystal becomes tetragonal and the critical vibrations split into two branches. The spectrum of one is given by the first of Eqs. (15), i.e., by Eq. (26) with the replacement $a_+ \rightarrow a_-$. The spectrum of the second branch is given by the second of Eqs. (15), and for not too small $k > \omega_0/c$ it is of the form

$$\omega^2 = \omega_0^2[k^2\delta + (T_C - T)(a_- \cos^2\theta + b_- \sin^2\theta)] \tag{28}$$

where θ is the angle between **k** and the tetragonal axis.

Let us now consider a uniaxial transition where the crystal is tetragonal both above and below T_C. In this case, $\epsilon_{\perp}$ for small k, ω, and $T - T_C$ is a constant of order unity, and only $\epsilon_{\parallel}$ is singular near T_C. The vibrations which are critical in this case are those described by the second of Eqs. (15) from which we obtain

$$\omega^2 = \frac{k^2\delta + a_{\pm}|T - T_C| + \varepsilon_{\perp}^{-1}\operatorname{ctg}^2\theta}{\omega_0^{-2} + (ck\sin\theta)^{-2}}. \tag{29}^*$$

The spectrum of these excitations has the same k dependence as that shown in Fig. 2, but is sharply anisotropic. Critical vibrations occur only for a

---

*ctg ≡ cot.

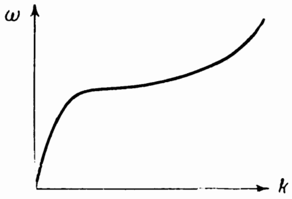

FIG. 2

narrow range of directions of **k**, almost perpendicular to the tetragonal axis.

For biaxial transitions when the atom is displaced in the yz plane, $\epsilon_{\|}$ is constant above the transition and $\epsilon_{\perp}$ is given by an equation of the form of (24). The first of Eqs. (15) yields an isotropic form of the spectrum of the form (26), and the second yields a spectrum of the form (29) with the replacement $\theta \rightarrow \pi/2 - \theta$. Below the transition both branches are anisotropic.

The correspondence between the quantum and classical results will be followed on the example of Eq. (27), from which the electromagnetic interaction, which has not been taken into account in the classical treatment, has dropped out. Equation (27) is of the same form as (11). The parameters entering in (27) go over into the classical expressions, since the case of classical statistics corresponds to temperatures much larger than the essential energy differences. The differences $(n_\mu - n_\nu)\omega_{\nu\mu}^{-1}$ in (22)—(25) go over into βn_ν and $\Pi_{\|}(0, T)$—into $\beta \overline{x^2}(T)$. In the case of the single-well potential of Fig. 1a the differences $\omega_{\nu\mu}$ go over in the classical limit into the frequencies $n\omega_H$, the matrix elements $x_{\mu\nu}$ go over into the Fourier components $x_n(H)$,[8] and (27) goes over into (11).

In the quasiclassical case of the double-well potential of Fig. 1b the energy differences of the even and odd states $\omega_{as}(\nu)$ are exponentially small for energies lower than the barrier height. If in summing over μ and ν in (22) we separate these pairs of states into a separate term, then in the region of frequencies ω much larger than ω_{as}, the quantum formula for the spectrum analogous to (27) will go over into the classical Eq. (13) and will correspond to a noncritical branch of vibrations. In this case vibrations of low frequencies $\omega \ll \omega_{as}$ will be critical. The main contribution to (25) for ω_0 is due to transitions between states of various symmetries whose energies are lower than the barrier height:

$$\omega_0^{-2} = \frac{2V_0^2}{\lambda} \sum_\nu n_\nu \frac{x_0^2(\nu)}{\omega_{as}^2(\nu)}, \qquad (30)$$

where $x_0(\nu)$ is the average value of x over the region of one of the wells. The frequency given by (27) may turn out to be small compared with the frequencies of the relaxation whose effect is discussed below. For small penetrability there may, therefore, exist no critical vibrations in order-disorder transitions.

If the barrier penetrability is not small, then critical vibrations should also appear in order-disorder transitions.

5. THE EFFECT OF RELAXATION PROCESSES

As has already been noted, below the transition point expression (24) for $\epsilon(0, \omega)$ does not go over at low frequencies into its static value ϵ_{st} which can be obtained by differentiating the average dipole moment with respect to the external field

$$\varepsilon_{st} = 1 + 4\pi \frac{\partial P_x}{\partial E_x} = 1 + \frac{\lambda \Pi_{st}}{1 - V_0 \Pi_{st}},$$

$$\Pi_{st} = \sum_{\mu \neq \nu} \frac{n_\mu - n_\nu}{\omega_{\nu\mu}} x_{\mu\nu}^2 + \beta \sum_\nu n_\nu (x_{\nu\nu} - s)^2. \qquad (31)$$

This is due to the fact that relaxation processes which lead to static equilibrium have not been taken into account above. Phenomenologically their effect can be allowed for by the Mandel'shtam-Leontovich method,[10] by introducing in Eq. (16) for the density matrix a term that describes the relaxation of the distribution of the atoms in the unit cell to a Gibbs distribution with a given instantaneous value of the acting field E_i:

$$i \frac{\partial \rho_i}{\partial t} = [H_i, \rho_i] - \frac{i}{\tau}\left(\rho - \frac{e^{-\beta H_i}}{\mathrm{Sp}\, e^{-\beta H_i}}\right), \qquad (32)$$

where τ is the relaxation time. Carrying out the calculations by the same method as above, we obtain for the permittivity Eqs. (21) in which $\Pi_{\alpha\beta}$ is given, instead of by (22), by the expression

$$\Pi_{\alpha\beta}(\omega, T) = \sum_{\mu, \nu} x_{\mu\nu}{}^\alpha x_{\nu\mu}{}^\beta \frac{(n_\mu - n_\nu)(1 + i/\tau\omega_{\nu\mu})}{\omega_{\nu\mu} + \omega + i/\tau} - \beta \frac{s^\alpha s^\beta}{1 - i\omega\tau}. \qquad (33)$$

In the low-frequency case $\omega \ll \omega_{\nu\mu}$ of interest to us

$$\Pi_{\|} = \Pi_{st} + \frac{i\omega\tau}{1 - i\omega\tau} \beta \sum_\nu n_\nu (x_{\nu\nu} - s)^2. \qquad (34)$$

Above the transition $x_{\nu\nu} = 0$ and $s = 0$, and $\Pi_{\|}$ coincides with the static value Π_{st}. For $\omega\tau \gg 1$ below T_C, the value of $\Pi_{\|}$ is given by (22) with $\omega = 0$, and only for $\omega\tau \ll 1$ does it go over into its static value (31). Therefore in the equation for the dielectric permittivity near the transition $\epsilon_{\pm}(\omega) = C_{\pm}(\omega)|T - T_C|^{-1}$ below T_C the Curie constant $C_-(\omega)$ will depend on the frequency, and for frequencies $\omega > \tau^{-1}$ the ratio of the constants C_+ to $C_-(\omega)$ should exceed the static value of 2.

The use of the introduced phenomenological relaxation time τ can yield only a qualitative description. Apparently τ should be considered a quantity of the order of the damping time of optical phonons; the dispersion connected with it should, therefore, be observed in the region of centimeter or millimeter waves. The decrease of $C_-(\omega)$ with frequency observed experimentally in a number of cases[11,12,5] can be related to several mechanisms: the piezoelectric effect,[11] domain relaxation, etc. The excess of the ratio C_+/C_- over 2 is to some extent also due to the fact that the vibrations are adiabatic, and not isothermal.[5] In comparing the results with experiments one must, therefore, take into account that the observed dispersion which also exists in a clamped, single-domain crystal is connected only with one of the possible mechanisms.

The effect of the relaxation turns out to be most noticeable in order-disorder transitions in the case of small barrier penetrability. In this case, as has been noted in Sec. 4, the frequencies of the relaxation τ^{-1} and ω can turn out to be higher than the exponentially low transition frequencies ω_{as}. Taking into account that τ^{-1} and ω are much smaller than the remaining transition frequencies $\omega_{\nu\mu}$ and $\beta\omega_{\mathrm{as}} \ll 1$, we obtain in this case for Π

$$\Pi_{\parallel} = \Pi_{st} + \frac{i\omega\tau}{1 - i\omega\tau}\beta\left[2\sum_{\nu} n_\nu x_0^2(\nu) + \sum_{\nu} n_\nu (x_{\nu\nu} - s)^2\right], \tag{35}$$

where $x_0(\nu)$ is the same as in (30).

Near the transition dispersion of the susceptibility will occur for small values of $\omega\tau$. In this region

$$\varepsilon = \frac{C_\pm}{|T - T_C| - i\omega\tau B_\pm}, \qquad B_\pm = \frac{2V_0^2}{\lambda T_C} C_\pm \sum_{\nu} n_\nu x_0^2(\nu). \tag{36}$$

It is seen from (36) that on approaching T_C the dispersion of the permittivity starts at low frequencies $\omega \sim |T - T_C|(\tau B)^{-1}$; this corresponds to an increase in the effective relaxation time. At higher frequencies $\epsilon(\omega)$ is a smooth function of the temperature. A dependence of this kind has been observed in a number of experiments.[11,13]

6. DIAGRAM TECHNIQUE. DAMPING OF EXCITATIONS

In order to calculate the following self-consistent field approximations and also in order to justify more rigorously the graphic method which has been presented, it is convenient to make use of diagram-technique methods.[14] This technique is worked out for the case of Fermi and Bose statistics when the Hamiltonian is written in terms of second-quantization operators. In terms of these operators the Hamiltonian of the system under consideration is written in the form

$$\mathscr{H} = \int d\mathbf{r}\, \psi^+(\mathbf{r}) \left[-\frac{\Delta}{2m} + U(\mathbf{r})\right] \psi(\mathbf{r}) - \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \psi^+(\mathbf{r}) \psi^+(\mathbf{r}') V(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') \psi(\mathbf{r}). \tag{37}$$

For what follows it is essential to make use of the circumstance that each unit cell contains with overwhelming probability one and only one atom. This condition it is most convenient to write by adding to the Hamiltonian the term

$$g \sum_i \left(\int_{\mathrm{un}^i} \psi^+(\mathbf{r}) \psi(\mathbf{r})\, d\mathbf{r} - 1 \right)^2. \tag{38}$$

Here the sum is over all unit cells, the integral—over the volume v_{un} of a unit cell, and the constant g will in the answers tend to infinity. Addition to (37) of the term (38) does not change the form of the Hamiltonian, and one can use the usual methods of calculation.

Taking as the zeroth interaction representation Hamiltonian the first term of (37), one can separate the uncoupled graphs. The coupled graphs can be represented in the form of one-cell blocks, connected by dashed lines, which correspond to the second term in (37). When taking into account the electromagnetic interaction, the dashed line represents the sum of the interaction V and the zeroth Green's function of the photon.

Graphs of all orders in the interaction (38) are collected in each block. In calculating a single-cell block, one can let g in (38) go to infinity. This reduces the problem to the one-particle case. In addition to the first term of (37), it is convenient to include in the one-particle Hamiltonian also the zeroth self-consistent field approximation from the second term; it coincides then with H_0 from (18).

For the interaction which we are considering $V_R(\mathbf{r}, \mathbf{r}') = (\mathbf{r} \cdot \mathbf{r}')V_R$; the Fourier component of a single-cell block with n outgoing lines is given by

$$\Gamma_n^{\alpha_1,\alpha_2\ldots\alpha_n}(\omega_1, \omega_2, \ldots, \omega_n) = T^n \int_0^\beta \prod_{j=1}^n dt_j e^{i\omega_j t_j} \left[\left\langle \hat{T} \prod_{j=1}^n x_{\alpha_j}(t_j) \right\rangle - \left\{ \hat{T} \prod_{j=1}^n x_{\alpha_j}(t_j) \right\}\right], \tag{39}$$

where $x(t) = e^{H_0 t} x e^{-H_0 t}$, $\hat{T}$ is the T-ordering symbol,[14] $i\omega_m = 2\pi i m T$ are the imaginary frequencies of the temperature diagram technique,[14] the average $\langle\ldots\rangle$ denotes $\mathrm{Sp}\,\rho_0(\ldots)$ with ρ_0 from (18), and the symbol $\{\ldots\}$ denotes the sum of the products of all possible averages of lower rank. For an oscillator potential U(r) it follows from the Wick theorem for Bose operators that only Γ_2 does not vanish in (39).

The Fourier component of the two-particle correlation function of the coordinates is expressed in terms of the irreducible part $\Pi_{\alpha\beta}$ with the aid of the formulas[1]

$$K_{\alpha\beta}(\mathbf{k}, i\omega_n) = \sum_{\mathbf{R}_{ij}} \int_0^\beta \langle (x_i^\alpha(0) - s^\alpha)(x_j^\beta(t) - s^\beta)\rangle e^{i\omega_n t - i\mathbf{k}\mathbf{R}_{ij}}$$

$$= \Pi_{\alpha\beta} + \sum_{\gamma=1} \Pi_{\alpha\gamma} V K_{\gamma\beta}, \tag{40}$$

and $\Pi_{\alpha\beta}$ is represented by the sum of the diagrams of Fig. 3, where the dashes denote the screening interaction $V_{\mathbf{k}}(1 - \Pi V_{\mathbf{k}})^{-1}$.

The diagram of Fig. 3a corresponds to the first self-consistent field approximation:

$$\Gamma_2^{\alpha\gamma}(\omega_{n_1}, \omega_{n_2}) = \delta(\omega_{n_1} + \omega_{n_2}) T \Pi_{\alpha\gamma}^{(0)}(i\omega_n),$$

$$\Pi_{\alpha\gamma}^{(0)}(i\omega_n) = \sum_{\mu\neq\nu} x_{\mu\nu}{}^\alpha x_{\nu\mu}{}^\gamma \frac{n_\mu - n_\nu}{\omega_{\nu\mu} + i\omega_n}$$

$$+ \beta\delta(\omega_n) \sum_\nu n_\nu (x_{\nu\nu}{}^\alpha x_{\nu\nu}{}^\gamma - s^\alpha s^\gamma). \tag{41}$$

Here $\delta(\omega_n)$ is the Kronecker symbol. The last term of (41) differs from zero only for $T < T_C$, and α and γ corresponding to the tetragonal axis. In deriving (41) use has been made of the relation

$$\left(\frac{n_\mu - n_\nu}{\omega_{\nu\mu} + i\omega_n}\right)_{\mu=\nu} = \delta(\omega_n)\beta n_\nu. \tag{42}$$

With the aid of the correlation function (40) one can find the correction to the free energy of the system[1]:

$$\beta F = \beta F^{(0)} + \frac{1}{2}\sum_{\mathbf{k}}\sum_n \ln(1 - V_{\mathbf{k}}\Pi_\parallel^{(0)}(i\omega_n))$$

$$+ \sum_{\mathbf{k}}\sum_n \ln(1 - V_{\mathbf{k}}\Pi_\perp^{(0)}(i\omega_n)), \tag{43}$$

where $F^{(0)}$ denotes the zeroth self-consistent field approximation.

Carrying out the analytic continuation of the function $K(i\omega_n)$ into the complex plane ω,[14] $i\omega_n \to \omega$, we arrive at formulas (21) for the dielectric permittivity. As has been noted above, for the oscillator potential U(r) only diagram a of Fig. 3 in Π does not vanish, and Eqs. (41) and (43) are exact.

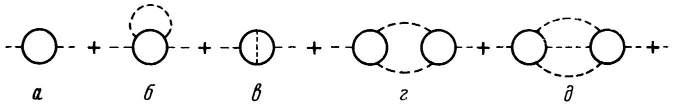

FIG. 3

In order to determine the corrections to the spectrum and the phonon damping, one must take into account the following approximations in Π, i.e., diagrams b—e of Fig. 3. Each integration over the momenta that enters into the dashed lines leads to a small factor, proportional to R_0^{-3}.[1] Thus diagrams b, c, and d are of the order R_0^{-3} and diagram e is of the order of R_0^{-6}. From parity considerations, diagram d differs from zero only below the transition. For simplicity, we will confine ourselves below to the region above the transition for the cubic case and not too small wave vectors $k > \omega_0/c$. As was shown in Sec. 4, one need not consider explicitly the effects of the electromagnetic interaction, and $\Pi_{\alpha\gamma}^{(0)}$ in (41) is of the form $\delta_{\alpha\gamma}\Pi_0$. For the first correction to Π which is of the form $\Pi_{\alpha\gamma}^{(1)} = \delta_{\alpha\gamma}\Pi^{(1)}$ we obtain

$$\Pi^{(1)}(i\omega_n) = \sum_{\gamma=1}^{3}\sum_m \beta^2\Gamma_4^{\alpha\gamma\gamma\alpha}(\omega_n, \omega_m, \omega_m, \omega_n)\sum_{\mathbf{q}} \frac{V_{\mathbf{q}}}{1 - V_{\mathbf{q}}\Pi_0(i\omega_m)}$$

$$\beta^2\Gamma_4^{\alpha_1\alpha_2\alpha_3\alpha_4}(\omega_1, \omega_2, \omega_3, \omega_4) = \sum_{\lambda\mu\nu\rho} \hat{P} x_{\lambda\mu}^{\alpha_1} x_{\mu\nu}^{\alpha_2} x_{\nu\rho}^{\alpha} x_{\rho\lambda}^{\alpha_4}$$

$$\times n_\lambda \frac{T\delta(\omega_1 + \omega_2 + \omega_3 + \omega_4)}{(\omega_{\lambda\mu} + i\omega_1)(\omega_{\lambda\nu} + i\omega_1 + i\omega_2)(\omega_{\lambda\rho} - i\omega_4)}$$

$$- \Gamma_2^{\alpha_1\alpha_2}(\omega_1, \omega_2)\Gamma_2^{\alpha_3\alpha}(\omega_3, \omega_4) - \Gamma_2^{\alpha_1\alpha_3}(\omega_1, \omega_3)\Gamma_2^{\alpha_2\alpha_4}(\omega_2, \omega_4)$$

$$- \Gamma_2^{\alpha_1\alpha_4}(\omega_1, \omega_4)\Gamma_2^{\alpha_2\alpha_3}(\omega_2, \omega_3). \tag{44}$$

Here the symbol P denotes the sum of all possible permutations of the indices 1, 2, 3, and 4.

The damping is determined by the imaginary part $\Pi(\omega)$ which appears in the analytic continuation of $\Pi(i\omega_n)$ to the real axis. In the case of the small frequencies $\omega \ll \omega_{\nu\mu}$ of interest to us the contribution to the imaginary part $\Pi^{(1)}$ in (44) will be due only to terms containing $\delta(\omega_n + \omega_m)$. Using relation (42) to separate these terms, we obtain

$$\operatorname{Im}\Pi^{(1)}(\omega) = \Gamma \int \frac{d\mathbf{q}}{(2\pi)^3}\delta(1 - V_{\mathbf{q}}\Pi_0(\omega)),$$

$$\Gamma = 8\pi V_0 \sum_{\substack{\lambda\neq\mu \\ \nu\neq\rho}} \frac{(x_{\lambda\mu}^{\alpha})^2}{\omega_{\lambda\mu}} \frac{(x_{\nu\rho}^{\alpha})^2}{\omega_{\nu\rho}} (\delta_{\lambda\nu} n_\nu - n_\lambda n_\nu). \tag{45}$$

Near the phase transition point, the excitation spectrum with account of (25) and (27) is of the form

$$\omega^2(\mathbf{k}) = \left(V_0 \frac{\partial\Pi_0}{\partial\omega^2}\right)^{-1} \left[\frac{k^2R_0^2}{6} + (T - T_C)\left(-\frac{\partial\Pi_0 V_0}{\partial T}\right) - i\alpha V_0 \Gamma \frac{kR_0}{\sqrt{6}}\right]. \tag{46}$$

Here $\alpha = 3\sqrt{6}/2\pi R_0^3$ is the small parameter of the self-consistent field expansion, the derivatives of Π_0 are taken at the point $\omega = 0$ and $T = T_C$, and small corrections $\sim\alpha$ to the real part of ω^2 have been omitted.

An appreciable contribution to the thermodynamic quantities is due to excitations with wave vectors for which the first and second term in (46) are of the same order of magnitude. It is seen from (46) that for these **k** the relative damping Im ω/Re ω is proportional to $\alpha(T - T_C)^{-1/2}$. Therefore at the limit of applicability of the self-consistent field method[1] $T - T_C \sim \alpha^2 T_C$ the damping becomes comparable with the frequency, and the vibrations disappear.

The damping described by (45) and (46) is connected with the scattering of phonons by density fluctuations and is small for long-wave excitations with $\mathbf{k} \to 0$. Diagram e of Fig. 3 describes, in addition to the scattering by fluctuations, also phonon-phonon interaction processes. The damping connected with these processes does not disappear for small **k** and can be found by the method described above. After analytic continuation in the frequency, the imaginary part of diagram e which corresponds to the scattering of a given phonon by one of the thermal phonons is given for small **k**, ω, and $T - T_C$ by the expression

$$\operatorname{Im}\Pi_{\alpha\beta}^{(2)} = \delta_{\alpha\beta} G^2 \omega \int \frac{d\mathbf{p}\,d\mathbf{q}}{(2\pi)^6} \frac{\delta(\omega + \omega_{\mathbf{p}} - \omega_{\mathbf{q}} - \omega_{\mathbf{k-p-q}})}{\omega_{\mathbf{p}}^2 \omega_{\mathbf{q}}^2 \omega_{\mathbf{k-p-q}}^2}. \tag{47}$$

Here G^2 is a constant proportional to the product of two vertices Γ_4 from (44) at zero frequencies, and $\omega_{\mathbf{k}}^2$ is given by the right-hand side of (46) or (27). In (47) it has been assumed that the frequencies ω and $\omega_{\mathbf{k}}$ are small compared with the temperature, so that the Bose distribution functions $n_i = (\exp \beta\omega_i - 1)^{-1}$ appearing in the calculations are replaced by the classical limit $(\beta\omega_i)^{-1}$.

Expression (47) is of the order of α^2, and for a real phonon with $\omega = \omega_{\mathbf{k}}$ differs from zero for all **k**. Thus for $T - T_C \lesssim \alpha^2 T_C$ the damping is comparable in order of magnitude with the frequency for all **k**.

7. ARBITRARY INTERACTION. TRANSITIONS IN OTHER SYSTEMS.

In order to simplify the equations, we assumed above a simple form of the interaction between the unit cells $V_R(\mathbf{r}_i, \mathbf{r}_j) = (\mathbf{r}_i \cdot \mathbf{r}_j)V_R$. We shall show that, as in thermodynamics,[15] all the results are retained for an arbitrary interaction.

Equations (16) take on the form

$$i\frac{\partial\rho_i}{\partial t} = [H_i, \rho_i], \quad H_i = \frac{p_i^2}{2m} + U(\mathbf{r}_i) - \sum_j \operatorname{Sp} V_{\mathbf{R}}(\mathbf{r}_i, \mathbf{r}_j)\rho_j - e_{\text{eff}}\,\mathbf{r}_i\mathbf{E}_i. \tag{48}$$

The equilibrium matrix ρ_0 is defined in analogy with (18):

$$\rho_i^0 = \frac{e^{-\beta H_{0i}}}{\operatorname{Sp} e^{-\beta H_{0i}}}, \quad H_{0i} = \frac{p_i^2}{2m} + U(\mathbf{r}_i) - \sum_j \operatorname{Sp}_j V(\mathbf{r}_i, \mathbf{r}_j)\rho_j^0. \tag{49}$$

We seek a solution of (48) in the form (17). In the representation of the eigenfunctions ψ_ν of the operator H_0 we obtain for the addition ρ linear in the field from (49) the equation

$$\rho_{\lambda\mu} = \sum_\alpha P_{\lambda\mu} x_{\lambda\mu}^\alpha E^\alpha + \sum_{\nu\sigma} P_{\lambda\mu} V_{\lambda\mu,\nu\sigma}^{\mathbf{k}} \rho_{\nu\sigma}, \quad P_{\lambda\mu} = \frac{n_\lambda - n_\mu}{\omega_{\mu\lambda} + \omega},$$

$$V_{\lambda\mu,\nu\sigma}^{\mathbf{k}} = \int \psi_\lambda(\mathbf{r})\psi_\mu(\mathbf{r}) V^{\mathbf{k}}(\mathbf{r}, \mathbf{r}')\psi_\nu(\mathbf{r}')\psi_\sigma(\mathbf{r}')\,d\mathbf{r}'\,d\mathbf{r}. \tag{50}$$

Expressing the solution of this equation in terms of the eigenfunctions ρ^m of the homogeneous equation

$$\lambda_m \rho_{\mu\nu}^m = P_{\mu\nu} \sum_{\sigma\tau} V_{\mu\nu,\sigma\tau}^{\mathbf{k}} \rho_{\sigma\tau}^m, \quad \sum_{\mu\nu} \rho_{\mu\nu}^m \frac{1}{P_{\mu\nu}} \rho_{\mu\nu}^n = \delta_{mn}, \tag{51}$$

we obtain for the dielectric permittivity by the usual method

$$\varepsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi e_{\text{eff}}^2}{v_{\text{un}}} \left[\sum_n \frac{\lambda_n}{1 - \lambda_n} \operatorname{Sp} x^\alpha \rho^n \cdot \operatorname{Sp} x^\beta \rho^n + \sum_{\mu\nu} x_{\mu\nu}^\alpha P_{\mu\nu} x_{\nu\mu}^\beta\right]. \tag{52}$$

The transition temperature T_C is defined in analogy with (23) and Eq. (33) of[15] as the point at which there appear for Eq. (49) solutions of the form $\rho^0 = \rho^{00} + \eta\rho^{01}$ where ρ^{01} describes a lower symmetry than ρ^{00} and $\eta \to 0$ for $T \to T_C - 0$:

$$\rho_{\mu\nu}^{01} = P_{\mu\nu}(T = T_C, \ \omega = 0) \sum_{\sigma\tau} V_{\mu\nu,\sigma\tau}^0 \rho_{\sigma\tau}^{01}. \tag{53}$$

If we normalize ρ^{01} in accordance with (51), then for T close to T_C and small ω and k, Eq. (51) for the functions ρ^1, which go over at $T = T_C$, $k = 0$, and $\omega = 0$ into ρ^{01}, can be solved by a method analogous to perturbation theory. Thus we obtain for the nondegenerate case

$$1-\lambda_1=\sum_{\substack{\mu\nu\\ \sigma\tau}}\rho_{\mu\nu}\left[\frac{P_{\mu\nu}(T_C,0)-P_{\mu\nu}(T,\omega)}{P^2_{\mu\nu}(T_C,0)}\delta_{\mu\nu,\sigma\tau}\right.$$

$$\left.+(V^0-V^{\mathbf{k}})_{\mu\nu,\sigma\tau}\right]\rho^{01}_{\sigma\tau}. \qquad (54)$$

Here the singular part of the dielectric permittivity is

$$\varepsilon_{\alpha\beta}=\frac{4\pi e^2_{\mathrm{eff}}}{v_{\mathrm{un}}}\frac{\mathrm{Sp}\, x^\alpha\rho^{10}\cdot\mathrm{Sp}\, x^\beta\rho^{10}}{1-\lambda_1}. \qquad (55)$$

Taking into account (54), we find that ϵ is of the form (24) where in the noncubic case k^2 may be replaced by some quadratic form of k_α. Only the expression of the parameters in terms of the interaction characteristics has thus changed in the dielectric constant.

If the transition is nonferroelectric, then the numerator in (55) vanishes, the dielectric permittivity has no singularities, and the critical vibrations are not related to the electromagnetic field. The spectrum of critical vibrations is in this case determined by the solution of the homogeneous equation for the addition to the density matrix, i.e., of Eq. (51) for $\lambda = 1$. For small k and ω the spectrum is determined by setting the right-hand part of equality (54) equal to zero, i.e., it is of the form (27). Here the anisotropy effects of the spectrum discussed in Sec. 4 and connected with the long-range action are absent, and the gap in the excitation spectrum is proportional to $|T - T_C|$ for all small k.

The collective excitations in second-order phase transitions connected with the ordering of the rotation of molecules in solids should exhibit peculiar characteristics. The assumption here is that above the transition the probabilities of arbitrary orientations of a molecule are equal, whereas below T_C there appears a preferred direction. For solids such a model is an idealization, since the presence of the crystal lattice always leads to anisotropy, but if the anisotropy is small then this model can be convenient for describing the phase transition. Using the methods described above, one can show that above T_C the spectrum of critical excitations is of the usual form (29), whereas below T_C there are two degenerate branches with an acoustic dispersion of the form ω = const · k, corresponding to vibrations relative to the direction of the spontaneous orientation.

Let us discuss the possibility of the existence of critical vibrations in other types of phase transitions.

Phase transitions of the ordering type in binary alloys are, as is well known,[16] described by the Ising model. In this model, there are not only no critical vibrations, but also no collective excitations and relaxation processes; since in this model an arbitrary distribution of spins in the unit cells is stationary, the Hamiltonian commutes with the operator σ_z^i of each unit cell. Excitations simply correspond to a reversal of the spin of an individual unit cell. Thus, in a cubic lattice with a nearest-neighbor interaction with a constant J, the excitation energies are 0, ± 4J, ± 8J, ± 12J, depending on the spin orientation of the neighbors, and depend neither on k nor on T.

Actually the relaxation of the distributions in binary alloys takes place by means of processes related to the temperature penetration of atoms through potential barriers, for instance by the diffusion of atoms along sites and along interstices. Introduction of the corresponding terms into the Hamiltonian allows one to describe relaxation processes.[17] However, critical excitations could exist only for an appreciable quantum penetrability of the barrier for exchange of positions of neighboring atoms of different kinds. In real alloys this penetrability is extremely small, and nonstationary processes connected with a redistribution of atoms in the unit cells are purely relaxation processes.

When applied to phase transitions in a superconductor, Bose-gas, and ferromagnet, the methods described above yield the known results. In a superconductor, the self-consistent field approximation is applicable at practically all temperatures.[1] The critical excitations correspond to moving Cooper pairs.[18,14] In a Bose system the "critical" excitations above T_C are the ordinary single-particle excitations and below T_C—it is the second Landau sound,[19] whose velocity vanishes at the transition like $(T_C - T)^{1/2}$, as the gap in the case of crystals. These results can be obtained by the method described, but for the Bose system the self-consistent field approximation coincides with perturbation theory,[1] and has no region of applicability in real liquid He^4. An investigation of spin waves in ferromagnets according to the described methods will be carried out in another paper.

8. CONCLUSION

We shall remark on the applicability of the results of the present study to real systems.

We have throughout the article discussed second-order phase transitions. There exist many first-order transitions which are "close to being second-order" in the sense that the thermodynamic quantities exhibit near the transition an anomalous temperature dependence, and the jumps characteristic of a first-order phase transition (for example, in the average displacement) are relatively small. The Curie temperature which enters in the Curie-Weiss equation for the dielectric permittivity is here below the transition temperature T_n for $T > T_n$ and above T_n for $T < T_n$. Therefore there may altogether not be any region $|T - T_C| \lesssim \alpha^2 T_C$ where the self-consistent field expansion is not applicable, and the anomalies connected with the transition are fully observable. An example are the numerous perovskite-type ferroelectrics which are well described by the phenomenological theory.[5] The equations and results of this paper can be directly generalized to this case if we understand T_C everywhere to denote the Curie temperatures T_C^+ and T_C^- which are different for regions above and below the transition.

The state of the unit cell has been described above by means of the coordinate of a single, chosen atom. In the general case, one must take into account the motion of all atoms of the unit cell. In all the formulas x^α is understood to be one or several generalized coordinates describing a group of atoms in the unit cell. In addition, one should take into account the interaction of the vibrations being considered with the remaining optical and acoustic phonons. As a result, there appears an additional damping, and also a renormalization of the interaction V.[20] Qualitative effects can only arise from the interaction via acoustic phonons which, like the electromagnetic interaction, is long-range.[21] It can be taken into account in the same way as the electromagnetic interaction was taken into account above, only instead of Maxwell's equations one must consider the equations of the theory of elasticity.[22]

In conclusion, we shall enumerate the main results of the present study. Critical vibrations can exist only for a large radius of interaction in the region in which the phenomenological theory of phase transitions is applicable. Even in this case, they do not appear in order-disorder transitions if the penetrability of the barrier is small. In ferroelectrics one should observe a dispersion of the dielectric permittivity at frequencies ω_r which decrease on approaching the transition point according to the law $\omega_r \sim |T - T_C|$; for large frequencies $\epsilon(\omega)$ ceases to follow the Curie-Weiss law.

In transitions of the displacement or order-disorder type for large barrier penetrability critical vibrations exist and have different spectra for cubic and noncubic ferroelectrics. In the cubic case, as in nonferroelectric transitions, the gap in the excitation spectrum near T_C tends to zero like $|T - T_C|$ independently of the orientation of the wave vector **k**. In a uniaxial transition the gap is small only in a narrow region of directions of **k**, almost perpendicular to the ferroelectric axis.

---

[1] V. G. Vaks, A. I. Larkin, and S. A. Pikin, JETP **51**, 361 (1966), Soviet Phys. JETP **24**, 240 (1967).

[2] V. L. Ginzburg, JETP **19**, 36 (1949); UFN **38**, 490 (1949).

[3] P. Anderson, Physics of Dielectrics, Trans. Second All-union Conf., AN SSSR, 1960, p. 290.

[4] W. Cochran, Phys. Rev. Letters **3**, 412 (1958); Adv. Phys. **9**, 387 (1960).

[5] F. Iona and D. Shirane, Ferroelectric Crystals, Pergamon, 1962.

[6] L. D. Landau and E. M. Lifshitz, Mekhanika (Mechanics), Nauka, 1965, Sec. 49.

[7] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media), Gostekhizdat, 1957.

[8] L. D. Landau and E. M. Lifshitz, Kvanotvaya mekhanika (Quantum Mechanics), 2nd ed., Fizmatgiz, 1963.

[9] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964, Sec. 119; L. D. Landau and E. M. Lifshitz, Mekhanika

[10] L. D. Landau, JETP M. Lifshitz, Mekhanika sploshnykh sred (Mechanics of Continuous Media), Gostekhizdat, 1953, Sec. 78.

[11] R. M. Hill and S. K. Ichiki, Phys. Rev. **128**, 1140 (1962); **132**, 1603 (1963).

[12] V. M. Petrov, Kristallografiya **6**, 632 (1961), Soviet Phys. Crystallography **6**, 508 (1962).

[13] H. Akao and T. Sasaki, J. Chem. Phys. **23**, 2210 (1955).

[14] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, 1962.

[15] V. G. Vaks, A. I. Larkin, and S. A. Pikin, Preprint, IAE-1067, 1966.

[16] M. A. Krivoglaz and A. A. Smirnov, Teoriya uporyadochivayushchikhsya splavov (Theory of Ordered Alloys), Fizmatgiz, 1958.

[17] G. H. Vineyard, Phys. Rev. **102**, 981 (1956).

[18] V. G. Vaks, V. M. Galitskiĭ, and A. I. Larkin, JETP **41**, 1655 (1961), Soviet Phys. JETP **14**, 1177 (1961).

[19] L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred (Mechanics of Continuous Media), Gostekhizdat, 1953, Sec. 130.

[20] V. G. Vaks and A. I. Larkin, JETP 49, 975 (1965), Soviet Phys. JETP 22, 678 (1966).

[21] M. A. Krivoglaz, FTT 5, 3437 (1963), Soviet Phys. Solid State 5, 2526 (1964).

[22] L. D. Landau and E. M. Lifshitz, Teoriya uprugosti (Theory of Elasticity), Nauka, 1965, Secs. 10 and 23.

Translated by Z. Barnea
192