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PHASE TRANSITIONS OF THE DISPLACEMENT TYPE IN FERROELECTRICS

V. G. VAKS

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A microscopic description is presented of the statistics and dynamics of phase transitions of the displacement type in ferroelectrics. The coefficients of the Devonshire expansion of the free energy are expressed in terms of microscopic parameters. The correlation effects in the transition region are considered. The spectrum of the low-frequency oscillations above and below the transition point is obtained.

INTRODUCTION

PHASE transitions in ferroelectrics are usually divided into two classes: of the order-disorder type and of the displacement type[1]. In order-disorder transitions, for example in KH_2PO_4 or triglycin sulfate, the ions and radicals which determine the polarization of the crystal have several (usually two) symmetrical equilibrium positions in the cell. These positions are quite far from each other, so that the total potential in which the ion moves is strongly anharmonic. These positions are statistically uniformly populated above the Curie temperature T_c, and a spontaneous asymmetry of the population, leading to polarization, appears below T_c. The character of the phase transition is in this case the same as in the well-known Ising model[2]; in particular, the transition is usually of second order. A theoretical description of order-disorder transitions encounters the usual difficulties of taking into account strong correlations in second-order phase transitions, it being necessary in this case to take into account also the influence of the long-range forces of the dipole-dipole interaction[3]. However, the dynamic effects connected with the possibility of nonrelaxation oscillations of the ion between the equilibrium positions are usually exponentially small[4], and the high-frequency dynamics of the crystal has no singularities near T_c[4,5].

Transitions of the displacement type, which are peculiar to ferroelectrics of the oxygen-octahedral type[1] such as $BaTiO_3$, are characterized by the fact that the anharmonicity of the potential has, for all the ions, the small order of magnitude that is usual for crystals. The phase transition takes place at ordinary temperatures T that are small compared with atomic energies ϵ_{at}, owing to the special cancellation, typical for these structures, of the terms that determine the rigidity against the given deformation of the cell[6,7]. The smallness of the anharmonicity makes it possible to describe the transition by the usual methods of expanding in powers of the ratio of the oscillation amplitudes to the cell dimensions, i.e., $T\epsilon_{at}^{-1}$. In this connection, as will be shown below, the correlation effects characteristic of second-order phase transitions are also proportional to $T\epsilon_{at}^{-1}$ and are small everywhere, except at temperatures very close to the point of the second-order phase transition T_c. Since, on the other hand, in transitions of the displacement type a first-order transition usually takes place before T_c is reached, there is no dangerous region and the expansion in powers of the anharmonicity is valid for all values of T. In thermodynamics this leads to the Devonshire expansion in powers of the polarization[8], and in dynamics it corresponds to the existence of a critical oscillation, called the Cochran oscillation, with a small and strongly-temperature-dependent gap in the energy spectrum[7,9-12,4].

The foregoing considerations, which were developed in papers by a number of workers[6-13], make it possible to construct a quantitative theory of a displacement-type transition, starting from microscopic considerations. This is precisely the purpose of the present paper. Inasmuch as the anharmonic terms play a decisive role in the transition, in this case there is a rare opportunity of directly determining the microscopic anharmonicity parameters in term of macroscopic quantities. The same constants determine here both the thermodynamics and the dynamics of the system in the region of small wave vectors k, a region important for the critical phenomena near the transition. Therefore the microscopic approach should make it possible to relate the thermodynamic properties with such dynamic characteristics as the temperature dependence of the frequency and the width of the critical oscillation, the dielectric losses at high and ultra-high frequencies, the probability of the Mossbauer effect near the transition, etc.

The microscopic approach to the thermodynamics of ferroelectrics of the displacement type was developed in a paper by Kwok and Miller[8] who derived an expression for the phenomenological parameters of the Devonshire expansion in terms of microscopic quantities. Certain problems, however, particularly the thermodynamic contribution of the critical degrees of freedom and the correlation effects, were not considered in[8]. In addition, they discarded in their microscopic expressions a number of terms which in general have the same order of magnitude as the retained terms. We therefore obtain in Secs. 3 and 4 a more accurate microscopic expression for the Devonshire coefficients, and discuss the correlation effects. The main purpose of the paper, on the other hand, is an analysis of the dynamics in the transition region. In Sec. 5 we obtain with the aid of a general expression for the phonon Green's function, equations for the oscillation spectrum of the system in the region of small k, with allowance for the connection between the acoustic and optical degrees of freedom and the piezoelectric effect. Thus, we present a microscopic derivation of the phenomenological equations of Ginzburg[9,14] and Cochran[10,11] and their generalization to the case of non-zero values of k in the region below the transition. From these equations we find an expression for the spectrum of the critical oscillations. A strong mutual influence of the critical and acoustic branches, leading to an unusual form of the spectrum of these oscillations at small k, is noted. It is found that in perovskites the spectrum of five low-lying branches at small values of k are determined by six constants, so that its experimental study makes it possible to determine these important characteristics of the crystal. The temperature dependence of the quadratic displacement of the ions and the Mossbauer effect near the transition will be considered in another paper.

We consider an ideal single-domain crystal. For concreteness, we discuss the case of perovskite, but the generalization to other cases is obvious. We use the temperature diagram technique[15], which is the most compact method of simultaneously describing the statistical and dynamic properties. The method and the qualitative results, including the existence of critical oscillations, are applicable also to the case of nonferroelectric transitions of the displacement type[9,4].

2. HAMILTONIAN AND DIAGRAM TECHNIQUE

As usual, we consider a crystal in the adiabatic approximation, assuming that the energy of the system is determined completely by specifying the coordinates and velocities of the ion centers. Then, expanding in usual fashion the energy in powers of the deviations of the ions from the equilibrium positions in the cubic phase[7,8], we have for the Hamiltonian the expression

$$H = \frac{1}{2}\sum_{i\mathbf{r}} m_i (\dot{\mathbf{u}}_{\mathbf{r}}^{i})^2 + \frac{1}{2}\sum_{\substack{i_1 i_2\\ \mathbf{r}_1\mathbf{r}_2}} \Phi^{\alpha_1 i_1 \alpha_2 i_2}(\mathbf{r}_1 - \mathbf{r}_2)\, u_{\mathbf{r}_1}^{\alpha_1 i_1} u_{\mathbf{r}_2}^{\alpha_2 i_2} - \sum_{i\mathbf{r}} e_i \mathbf{u}_{\mathbf{r}}{}^{i}\mathbf{E}_{\mathbf{r}}$$
$$+ \frac{1}{8\pi}\int (\mathbf{E}^2 + \mathbf{H}^2)\, dV + \sum_{n=3}^{\infty} \sum_{\substack{i_1\ldots i_n\\ \mathbf{r}_1\ldots\mathbf{r}_n}} \frac{1}{n!}\Phi^{\alpha_1 i_1\ldots\alpha_n i_n}(\mathbf{r}_1, \ldots, \mathbf{r}_n)\, u_{\mathbf{r}_1}^{\alpha_1 i_1} \ldots u_{\mathbf{r}_n}^{\alpha_n i_n}. \qquad (1)$$

Here $\mathrm{u}_{\mathbf{r}}^{\mathrm{i}}$ and $\dot{\mathrm{u}}_{\mathbf{r}}^{\mathrm{i}}$ are the displacement and the velocity operator of the i-th ion in the cell, characterized by the lattice vector $\mathbf{r} = \mathrm{n}_1\mathbf{a}_1 + \mathrm{n}_2\mathbf{a}_2 + \mathrm{n}_3\mathbf{a}_3$; $\mathbf{a}_\sigma$ are the fundamental periods, which form in this case a Cartesian triad of vectors; Φ are the coefficients in the expansion of the potential energy. The interaction $\Phi^{\alpha_1 \mathrm{i}_1 \alpha_2 \mathrm{i}_2}$ $(\mathbf{r}_1 - \mathbf{r}_2)$ includes only the short-range forces, particularly the difference between the field acting on the ion and the average field, but does not contain terms corresponding to the long-range dipole-dipole interaction. These facts are described with the aid of the average macroscopic field **E**, regarded as an independent dynamic variable; $\mathrm{e_i}$ is the effective charge of the ion, and by virtue of the neutrality of the cell we have $\sum_{\mathrm{i}} \mathrm{ei} = 0$. The coefficients Φ satisfy the known relations that follow from the invariants of the energy of the crystal under homogeneous displacement $\mathrm{u}_{\mathbf{r}}^{\alpha\mathrm{i}} \rightarrow \mathrm{u}_{\mathbf{r}}^{\alpha\mathrm{i}} + \mathrm{const}$:

$$\sum_{i_1\mathbf{r}} \Phi^{\alpha_1 i_1 \alpha_2 i_2}(\mathbf{r}) = \sum_{i_2\mathbf{r}} \Phi^{\alpha_1 i_1 \alpha_2 i_2}(\mathbf{r}) = 0,$$
$$\sum_{i_m\mathbf{r}_m} \Phi^{\alpha_1 i_1\ldots\alpha_m i_m\ldots\alpha_n i_n}(\mathbf{r}_1, \ldots, \mathbf{r}_m, \ldots, \mathbf{r}_n) = 0. \qquad (2)$$

After the usual changeover to Fourier components

$$\mathbf{u}_{\mathbf{k}}{}^{i} = \frac{1}{\sqrt{N}}\sum_{\mathbf{r}} \mathbf{u}_{\mathbf{r}}{}^{i} e^{-i\mathbf{k}\mathbf{r}}, \qquad \Phi^{\alpha_1 i_1 \alpha_2 i_2}(\mathbf{k}) = \sum_{\mathbf{r}} \Phi^{\alpha_1 i_1 \alpha_2 i_2}(\mathbf{r})\, e^{-i\mathbf{k}\mathbf{r}},$$
$$\mathbf{E}_{\mathbf{k}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{r}} \mathbf{E}_{\mathbf{r}} e^{-i\mathbf{k}\mathbf{r}}, \qquad (3)$$

where $\hbar \mathrm{k}$ is the quasimomentum and N is the number of cells, the Hamiltonian (1) takes the form

$$H = H_0 + H_{int} = \frac{1}{2}\sum_{\mathbf{k}}\Big[\sum_i (m_i \dot{\mathbf{u}}_{\mathbf{k}}{}^{i}\dot{\mathbf{u}}_{-\mathbf{k}}^{i} - 2e_i \mathbf{u}_{\mathbf{k}}{}^{i}\mathbf{E}_{-\mathbf{k}})$$
$$+ \sum_{ij} \Phi^{\alpha i\beta j}(\mathbf{k})\, u_{\mathbf{k}}^{\alpha i} u_{-\mathbf{k}}^{\beta j} + \frac{v_c}{4\pi}(\mathbf{E}_{\mathbf{k}}\mathbf{E}_{-\mathbf{k}} + \mathbf{H}_{\mathbf{k}}\mathbf{H}_{-\mathbf{k}})\Big] + H_{int}. \qquad (4)$$

Here $\mathrm{v_c}$ is the volume of the unit cell and $\mathrm{H_{int}}$ denotes the last term of (1), expressed in terms of $\mathrm{u}_{\mathrm{k}}^{\mathrm{i}}$. We are not interested here in the shortwave electromagnetic radiation with wavelength of the order or smaller than the cell dimension (the x-ray region), so that we can confine ourselves to the use of the field values at the lattice sites as the dynamic variables of the field. In this connection, the components $\mathbf{E}_{\mathrm{k}}$ are defined in (3) just as $\mathrm{u_k}$, and a factor $\mathrm{v_c}$ appears in the next to the last term of (4).

The quadratic expression in the square brackets of (4) can be reduced in the usual manner to the diagonal form corresponding to noninteracting phonons[8]. However, bearing in mind an application to the study of the spectra at small values of k and at small displacements of the individual ions, it is more convenient to perform this transformation in the following manner. We choose as the "acoustic" variable the coordinate $\mathrm{u}_{\mathrm{k}}^{1} \equiv \mathrm{u_k}$ of the given ion, and introduce in place of the remaining $\mathrm{u^i}$ the relative coordinates $\mathrm{y^i = u^i - u}$. We then make a canonical transformation of the "optical" variables $\mathrm{y}_{\mathrm{k}}^{\mathrm{i}}$ with coefficients independent of k, in such a way that when k = 0 the terms of the Hamiltonian $\mathrm{H_0}$ in (4) which are quadratic in **y** and $\dot{\mathbf{y}}$ take on the diagonal form:

$$y_{\mathbf{k}}^{i\alpha} = \frac{1}{\sqrt{m_i}}\sum_j e_j{}^{i\alpha} x_{\mathbf{k}}{}^{j},$$
$$\sum_i m_i (\dot{\mathbf{y}}_0{}^{i})^2 + \sum_{il} \Phi^{i\alpha l\beta}(0)\, y_0^{i\alpha} y_0^{l\beta} = \sum_j (\dot{x}_{j0}{}^2 + \lambda_j x_{j0}{}^2). \qquad (5)$$

In our case of perovskites with five ions per cell, the index j in (5) runs through twelve values. As noted by Kwok and Miller[8], owing to the cubic symmetry of the twelve quantities, the λ_{i} in (5) constitute four triply-degenerate groups λ_{b} (b = 1, 2, 3, 4), and for each b the three unit vectors $\mathrm{e_j = e_{b\sigma}}$ correspond to three polarizations of σ along the principal axes of the crystal:

$$e_{b\sigma}{}^{i\alpha} = v_i(b)\,\delta_{\alpha\sigma}, \qquad \mathbf{y}_{\mathbf{k}}{}^{i} = \sum_b \frac{v_i(b)}{\sqrt{m_i}}\mathbf{x}_{b\mathbf{k}}, \qquad (\mathbf{x}_{b\mathbf{k}})_\sigma = x_{\mathbf{k}}{}^{b\sigma}. \qquad (6)$$

After these transformations are performed, the Hamitonian (4) takes the form

$$H_0 + H_{int} = \frac{1}{2}\sum_{\mathbf{k}}\Big[\mathscr{M}\dot{\mathbf{u}}_{\mathbf{k}}\dot{\mathbf{u}}_{-\mathbf{k}} + \mathbf{u}_{\mathbf{k}} A \mathbf{u}_{-\mathbf{k}} + \frac{v_c}{4\pi}(\mathbf{E}_{\mathbf{k}}\mathbf{E}_{-\mathbf{k}} + \mathbf{H}_{\mathbf{k}}\mathbf{H}_{-\mathbf{k}})$$
$$+ \sum_b (2\dot{\mathbf{u}}_{-\mathbf{k}}\sqrt{\mu_b}\,\dot{\mathbf{x}}_{b\mathbf{k}} + 2\mathbf{u}_{-\mathbf{k}} V_b \mathbf{x}_{b\mathbf{k}} - 2z_b \mathbf{E}_{-\mathbf{k}}\mathbf{x}_{b\mathbf{k}} + \dot{\mathbf{x}}_{b\mathbf{k}}\dot{\mathbf{x}}_{b-\mathbf{k}} + \lambda_b \mathbf{x}_{b\mathbf{k}}\mathbf{x}_{b-\mathbf{k}})$$
$$+ \sum_{b,b'} \mathbf{x}_{b\mathbf{k}} S_{bb'} \mathbf{x}_{b'-\mathbf{k}}\Big] + H_{int}. \qquad (7)$$

We have introduced here the notation

$$\mathcal{M} = \sum_i m_i, \quad \sqrt{\mu_b} = \sum_i v_i(b)\sqrt{m_i}, \quad z_b = \sum_i e_i v_i(b) m_i^{-1/2},$$

$$A^{\alpha\beta}(\mathbf{k}) = \sum_{ij} \Phi^{i\alpha j\beta}(\mathbf{k}),$$

$$V_b{}^{\alpha\beta}(\mathbf{k}) = \sum_{ij} \Phi^{i\alpha j\beta}(\mathbf{k}) v_j(b) m_j^{-1/2},$$

$$S_{bb'}^{\alpha\beta}(\mathbf{k}) = \sum_{ij} v_i(b) v_j(b') m_i^{-1/2} m_j^{-1/2} \Phi^{i\alpha j\beta}(\mathbf{k}) - \lambda_b \delta_{bb'} \delta_{\alpha\beta}, \tag{8}$$

and the displacements u^i in the Hamiltonian H_{int} are expressed in terms of u and x_b.

The matrices A, V, and S in (7) and (8) vanish at small values of k. This follows from (2) and (3) for A and V and from (5) and (6) for S. Owing to the separation of the long-range electromagnetic forces into an individual term, the potentials $\Phi(\mathbf{k})$ and the matrices A, V, and S are analytic at small values of k. Therefore at values of k smaller than the reciprocal cell dimension $1/a$ the expansion of these matrices, with allowance for cubic and mirror symmetries, can be written in the form

$$\hat{A} = \mathcal{M} k^2 (a_l g^l + a_t g^t + a_a g^a), \quad \hat{V} = k^2 \sqrt{\mathcal{M}} (v_l g^l + v_t g^t + v_a g^a),$$

$$\hat{S} = k^2 (s_l g^l + s_t g^t + s_a g^a). \tag{9}$$

For brevity we have omitted here the indices b and b′ in the matrices V and S; a_i, v_i, and s_i are constants, and the tensors g^i depend only on components of the vector $\mathbf{n} = \mathbf{k}/k$:

$$g_{\alpha\beta}{}^l = n_\alpha n_\beta, \quad g_{\alpha\beta}{}^t = \delta_{\alpha\beta} - n_\alpha n_\beta, \quad g_{\alpha\beta}{}^a = \sum_{\sigma=1}^{3} e_\sigma{}^\alpha e_\sigma{}^\beta (\mathbf{n}\mathbf{e}_\sigma)^2, \tag{10}$$

where $\mathbf{e}_\sigma$ is the unit vector of the principal axis σ. In formulas (9) for A and V, the mass of the cell $\mathcal{M}$ is separated as a factor in order to reduce the quantities a_i, v_i, and s_k to one dimensionality—the square of the velocity. The constants a_i are then expressed as follows in terms of the elastic moduli c_{ik}:

$$a_l = (c_{12} + 2c_{44}) \frac{1}{\rho}, \quad a_t = \frac{c_{44}}{\rho}, \quad a_a = (c_{11} - c_{12} - 2c_{44}) \frac{1}{\rho}, \tag{11}$$

where $\rho = \mathcal{M}/v_c$ is the density. The quantities with the index a in (9) determine the degree of crystalline anisotropy, for example, a_a determines the elastic anisotropy of the crystal.

As noted by a number of authors[7,8], and as will become clear in what follows, the phase transition occurs at temperatures T much lower than the atomic energies ϵ_{at} only if one of the constants λ_b in (5) and (7), which we shall designate λ_c, is negative and small compared with the remaining λ_r, being a quantity on the order of $\lambda_r T \epsilon_{at}^{-1}$. The corresponding degree of freedom x_c will be called critical, and the others will be designated by the letter r. Owing to the smallness of λ_c, the critical degree of freedom at small values of k is strongly affected by anharmonic additions due to H_{int}, and also by the terms of V_c and S_{cc} which are proportional to k^2. For the remaining degrees of freedom, the anharmonic corrections can be neglected together with large values of λ_r.

We choose a transverse gauge for the potentials of the electromagnetic field: div A = 0, $\mathbf{A} = \mathbf{A}_t$. Then the dynamic variables in the Hamiltonian (7) will be the coordinates u and x_b, the scalar potential φ, and $\mathbf{A}_t$. Therefore, if we introduce the 18-component vector ξ_i with components $(\mathbf{u}, x_b, \varphi, \mathbf{A}_t)$, then the temperature Green's function of the system[15] can be written in the form of the matrix

$$G_{ij}(\mathbf{k}, i\omega_n) = \int_0^\beta d\tau e^{i\omega_n \tau} \sum_{\mathbf{r}_2} e^{i\mathbf{k}(\mathbf{r}_2 - \mathbf{r}_1)} \langle \hat{T}(\xi_i(\mathbf{r}_1, 0) - \bar{\xi}_i)(\xi_j(\mathbf{r}_2, \tau) - \bar{\xi}_j) \rangle. \tag{12}$$

Here $\beta = 1/T$, $\hat{T}$ is the symbol of the T-ordering[15], $i\omega_n = 2i\pi n T$ are the imaginary frequencies of the temperature diagram technique, $\xi_i(\tau) = e^{H\tau} \xi_i e^{-H\tau}$, $\bar{\xi}_i = \langle \xi_i \rangle$, and the mean value $\langle \ldots \rangle$ denotes the trace

$$\mathrm{Sp}\,[(\ldots) \exp(-\beta H)]\,[\mathrm{Sp} \exp(-\beta H)]^{-1}.$$

The zeroth Green's function G^0 corresponds to the Hamiltonian H_0 in (7) and is given, as usual, by the equation[15] $H_{ij}^0 G_{jl}^0 = \delta_{il}$, where H_{ij}^0 denotes the coefficient of $\frac{1}{2} \xi_i \xi_j$ in (7), with replacement of the time-derivative operator by the frequency, $d/dt \to \omega_n$, and with reversal of the sign in the diagonal term corresponding to the scalar potential[15] $H = -k^2 v_c (4\pi)^{-1}$. The explicit expression for the matrix G_0^{-1} is

$$G_0{}^{-1}(\mathbf{k}, i\omega_n) =$$

$$= \begin{pmatrix} \mathcal{M}\omega_n{}^2 + A & \omega_n{}^2 \sqrt{\mu_b} + V_b & 0 & 0 \\ \omega_n{}^2 \sqrt{\mu_b} + V_b{}^+ & \omega_n{}^2 + \lambda_b + S_{bb'} & i\mathbf{k} z_b & z_b \dfrac{\omega_n}{c} \\ 0 & -i\mathbf{k} z_b & -\dfrac{k^2 v_c}{4\pi} & 0 \\ 0 & -z_b \dfrac{\omega_n}{c} & 0 & \dfrac{v_c}{4\pi}\left(\dfrac{\omega_n{}^2}{c^2} + k^2\right) \end{pmatrix} \tag{13}$$

The first row and column correspond here to the displacements u, the second to x_b, the third to φ, and the fourth to $\mathbf{A}_t$; V^+ denotes the Hermitian conjugate of the matrix V. It is assumed that the wave vector k is much larger than the reciprocal dimension of the sample $1/L$, otherwise k must be understood to be an operator of differentiation with respect to the coordinate (see Sec. 5).

The anharmonic term in (7) can be written in the form

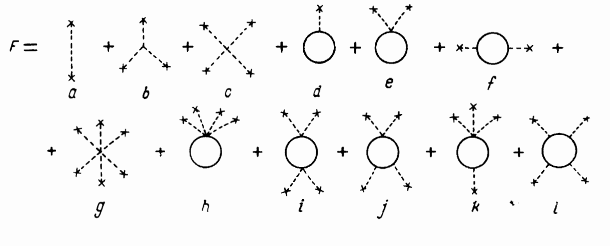
$$H_{int} = \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{i_1, i_2 \ldots i_n} \xi_{i_1} \xi_{i_2} \ldots \xi_{i_n} V_{i_1 i_2 \ldots i_n}^{(n)}. \tag{14}$$

A momentum index k_i is implied for each of the displacements ξ_i contained in (14), and the potentials $V_{i_1 \ldots i_n}^{(n)} = V_{i_1 \ldots i_n}^{k_1 \ldots k_n}$ differ from zero only if the total momentum equals the reciprocal lattice vector **b**: $\mathbf{k}_1 + \ldots + \mathbf{k}_n = \mathbf{b}$.

The diagram technique is constructed in the usual manner[13,15]. Each Green's function (11) corresponds on the diagram to a solid line, and each term $V^{(n)}$ of (14) corresponds to a vertex with n outgoing lines. In addition, just as in the case of an ideal Bose gas[15,8], it is necessary to separate among the optical degrees of freedom the non-zero mean values of the coordinates $\bar{x}_b$, and in the acoustic degrees of freedom the deformations $u_{\alpha\beta}$. Graphically these mean values will be represented by a cross from which a dashed line is drawn. After calculating the free energy F, the equilibrium value of the homogeneous displacements and deformations can be obtained from the condition that F be minimal.

3. CALCULATION OF THE FREE ENERGY

Taking into account the statements made in Sec. 2, the graphic expression for the density of the free energy F can be written in the form



(15)

In estimating the order of magnitude of the different terms in (15), we assume for concreteness that the phase transition occurs at temperatures larger than the Debye temperature Θ_D of the crystal, both in the majority of the perovskites and in BaTiO$_3$. We also take into account the fact that the deformations $u_{\alpha\beta}$ and the square of the spontaneous polarization P^2 have in atomic units the same order of magnitude as T, and the anomalous rigidity is $\lambda_c \sim \lambda_r T \epsilon_{at}^{-1}$. Then the first six terms a–f in the expansion (15) are of the order of T^2, and the remainder of the order T^3. These last terms could be neglected in the case of a "normal" second-order transition, when the temperature-independent constants in a–f and g–l have the same, atomic order of magnitude. However, the fact that the transition is a first-order one close to second-order transition, and the coefficient B of the fourth power of the polarization in the Devonshire expansion depends strongly on the temperature[1], indicates that B is anomalously small compared with the constants of the next approximation, and the corrections to B must be taken into account. The temperature addition to the other quantities, such as the elasticity coefficients or the electrostriction coefficients, can already be neglected[1]. This was taken into account when writing down the diagrams in (15), where we discarded, for example, loops with three outgoing dashed lines, since at least one of these dashed lines should correspond, from parity considerations, to the acoustic deformation $u_{\alpha\beta}$.

With the aid of (7) and (14) we can write the analytic expression corresponding to (15) in the form

$$F - F_0(T) = \frac{1}{2} c_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta} + \frac{1}{v_c} \sum_b \left(\frac{\lambda_b \bar{x}_b{}^2}{2} - z_b \bar{x}_b \bar{\mathbf{E}} \right) + \frac{\bar{\mathbf{E}}^2}{8\pi} + \xi_i \frac{\gamma_i T}{2v_c}$$
$$+ \bar{\xi}_i \bar{\xi}_j \frac{T d_{ij}}{4v_c} + \frac{\bar{\xi}_i \bar{\xi}_j \bar{\xi}_l}{3! v_c} V_{ijl}^{000} + \frac{\bar{\xi}_i \bar{\xi}_j \bar{\xi}_l \bar{\xi}_m}{4! v_c} \left(V_{ijlm}^{0000} + \frac{T e_{ijlm}}{2} \right) + \frac{\bar{\xi}_{i_1} \ldots \bar{\xi}_{i_6}}{6! v_c} V_{i_1 \ldots i_6}^{0 \ldots 0}. \tag{16}$$

Here $\mathbf{F}_0(\mathrm{T})$ denotes that part of the free energy which does not depend on the average displacements, and we have introduced the notation

$$\gamma_i = \sum_{\mathbf{k}n} V_{ii_1i_2}^{0\mathbf{k}-\mathbf{k}} G_{i_1i_2}^{\mathbf{k}n}, \quad d_{ij} = \sum_{\mathbf{k}n} \left(V_{iji_1i_2}^{00\mathbf{k}-\mathbf{k}} G_{i_1i_2}^{\mathbf{k}n} - V_{ii_1i_2}^{0\mathbf{k}-\mathbf{k}} V_{ji_3i_4}^{0\mathbf{k}-\mathbf{k}} G_{i_2i_3}^{\mathbf{k}n} G_{i_4i_1}^{\mathbf{k}n} \right),$$
$$e_{ijlm} = \sum_{\mathbf{k}n} [V_{ijlmi_1i_2}^{0000\mathbf{k}-\mathbf{k}} G_{i_1i_2}^{\mathbf{k}n} - (3V_{iji_1i_2}^{00\mathbf{k}-\mathbf{k}} V_{lmi_3i_4}^{00\mathbf{k}-\mathbf{k}} + 2V_{ijli_1i_2}^{000\mathbf{k}-\mathbf{k}} V_{mi_3i_4}^{0\mathbf{k}-\mathbf{k}}) G_{i_2i_3}^{\mathbf{k}n} G_{i_4i_1}^{\mathbf{k}n}$$
$$+ 6V_{iji_1i_2}^{00\mathbf{k}-\mathbf{k}} V_{li_3i_4}^{0\mathbf{k}-\mathbf{k}} V_{mi_5i_6}^{0\mathbf{k}-\mathbf{k}} G_{i_2i_3}^{\mathbf{k}n} G_{i_4i_5}^{\mathbf{k}n} G_{i_6i_1}^{\mathbf{k}n}$$
$$- V_{ii_1i_2}^{0\mathbf{k}-\mathbf{k}} V_{ji_3i_4}^{0\mathbf{k}-\mathbf{k}} V_{li_5i_6}^{0\mathbf{k}-\mathbf{k}} V_{mi_7i_8}^{0\mathbf{k}-\mathbf{k}} G_{i_2i_3}^{\mathbf{k}n} G_{i_4i_5}^{\mathbf{k}n} G_{i_6i_7}^{\mathbf{k}n} G_{i_8i_1}^{\mathbf{k}n}]. \tag{17}$$

The upper indices in the potential V indicate the values of the momenta; $G^{\mathbf{k}n} = G(\mathbf{k}, i\omega_n)$. Summation from 1 to 3 is implied over repeated Greek indices, and from 1 to 18 over Latin indices. The symbol $\bar{\xi}_i$ denotes simply the mean value $\bar{x}_b$ for the optical coördinates x_b, and the deformation $u_{\alpha\beta}$ for the acoustic coordinates. In the latter case, the zero index of the potential $V_{\alpha\ldots}^{0\cdots}$ denotes actually the limit as $\mathbf{k} \to 0$, corresponding to the derivative of this potential multiplied by $(-i)$[8]:

$$\lim_{\mathbf{k}\to 0} (u_{\mathbf{k}}{}^{\alpha} V_{\alpha\ldots}^{\mathbf{k}\ldots}) = \frac{1}{2} (u_{\mathbf{k}}{}^{\alpha} k^{\beta} + u_{\mathbf{k}}{}^{\beta} k^{\alpha}) \frac{\partial}{\partial k_\beta} V_{\alpha\ldots}^{\mathbf{k}\ldots} \Big|_{\mathbf{k}=0}$$
$$= u_{\alpha\beta} \left(-i \frac{\partial}{\partial k_\beta} V_{\alpha\ldots}^{\mathbf{k}\ldots} \right) \Big|_{\mathbf{k}=0} \tag{18}$$

inasmuch as the potential $V_{\alpha\ldots}^{0\cdots}$ itself vanishes as a result of (2).

It is important[7] in what follows that the significant region of the integrals with respect to k in (17) is that the significant region of the integrals with respect to k in (17) is that of large wave vectors $k \sim 1/a$, since the contribution of the region of small k is suppressed with a statistical weight $\sim k^3$. At these large values of k in the Green's function, the influence of λ_c and of the temperature-dependent anharmonic corrections becomes small even for the critical branch, since the coefficients s_i in (9) have, generally speaking, the normal atomic order of magnitude. Therefore in first approximation the function G in (17) can be replaced by $G^{00}(\mathbf{k}, i\omega_n)$, given by the matrix (13) at $\lambda_c = 0$. The influence of the next terms is discussed in Sec. 4. After making such a substitution, the quantities γ_i, d_{ij}, and e_{ijlm} in (17) are smooth functions of the temperature and are constant when $T > \Theta_D$, when it is possible to confine oneself to the classical term with n = 0 in the sums over n in (17).

To express F in terms of the polarization and deformation, we also take into account the fact[8] that the equilibrium displacement of the critical coordinate $\bar{x}_c$ is much larger than the remaining displacements $\bar{x}_r$, for when x_b is determined from the condition $\partial F/\partial \bar{x}_b = 0$ the displacements x_r are inversely proportional to the normal rigidities λ_r, and $\bar{x}_c$ is inversely proportional to the sum of λ_c and the anharmonic corrections $\sim \lambda_r T \epsilon_{at}^{-1}$. The polarization P per unit volume is accordingly determined by the coordinate x_c

$$\mathbf{P} = \frac{1}{v_c} \sum_b z_b \bar{x}_b \approx \frac{z_c \bar{x}_c}{v_c}. \tag{19}$$

As a result, (16) takes on the form of the Devonshire expansion[16,1]:

$$F - F_0(T) = \frac{c_{\alpha\beta\gamma\delta} u_{\alpha\beta} u_{\gamma\delta}}{2} - \gamma T u_{\alpha\alpha} + 2\pi P^2 \frac{T - T_c}{C_+} - \mathbf{PE} + \frac{E^2}{8\pi}$$
$$- q_{\alpha\beta\gamma\delta} P_\alpha P_\beta u_{\gamma\delta} + \frac{B_{11}}{4} \sum_\sigma P_\sigma{}^4 + \frac{B_{12}}{2} \sum_{\sigma>\sigma'} P_\sigma{}^2 P_{\sigma'}{}^2 + \frac{c_{111}}{6} \sum_\sigma P_\sigma{}^6$$
$$+ \frac{c_{112}}{2} \sum_{\sigma\neq\sigma'} P_\sigma{}^4 P_{\sigma'}{}^2 + c_{123} P_1{}^2 P_2{}^2 P_3{}^2. \tag{20}$$

According to (16)–(20), the expansion parameters are expressed in terms of the microscopic quantities as follows:

$$\gamma = \frac{i}{6}\frac{\partial}{\partial p_a}\sum_{\mathbf{k}n} V_{ij\alpha_a}^{-(\mathbf{p}+\mathbf{k})\mathbf{k}\mathbf{p}} G_{ij}^{\mathbf{k}n}\Big|_{\mathbf{p}=0} \qquad C_+ = \frac{2\lambda}{d_{11}}, \quad \lambda = \frac{4\pi z_c^2}{v_c}$$

$$T_c = -\frac{2\lambda_c}{d_{11}}, \quad q_{\alpha\beta\gamma\delta} = i\frac{v_c}{z_c^2}\frac{\partial}{\partial p_\delta} V_{\alpha\beta\gamma_a}^{0-\mathbf{p}\mathbf{p}}\Big|_{\mathbf{p}=0}, \quad B_{\alpha\beta} = b_{\alpha\beta} + Te_{\alpha\beta},$$

$$b_{11} = \frac{v_c^3 V_{1111}^{0000}}{6z_c^4} \quad b_{12} = \frac{v_c^3 V_{1122}^{0000}}{2z_c^4}, \quad e_{11} = \frac{v_c^3 e_{1111}}{12z_c^4}, \quad e_{12} = \frac{v_c^3 e_{1122}}{4z_c^4},$$

$$c_{111} = \frac{v_c^5 V_{111111}^{000000}}{120 z_c^6}, \quad c_{112} = \frac{v_c^5 V_{111122}^{000000}}{24 z_c^6}, \quad c_{123} = \frac{v_c^5 V_{112233}^{000000}}{8 z_c^6}. \tag{21}$$

The Greek indices with the symbol a at the potentials in (21) correspond to the acoustic degree of freedom, while the indices without the symbol correspond to the critical degree of freedom.

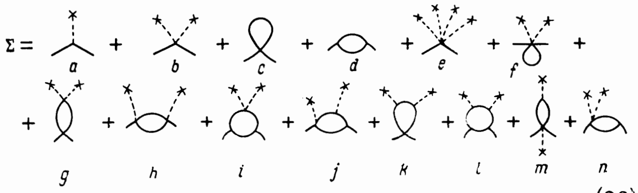
Formulas (20) and (21) differ from the results of Kwok and Miller[8] in that the coefficients $\gamma_1 d_{\alpha\beta}$, and $e_{\alpha\beta\gamma\delta}$ are expressed in terms of the microscopic parameters (17). In[8] these constants were calculated in the self-consistant-field approximation corresponding to discarding the terms f and i–l in the diagrams of (15). As noted above, the indicated diagrams have the same order of magnitude with respect to the parameter $T\epsilon_{at}^{-1}$ as the remaining ones. In addition, in the final expressions, which were analogous to (17), Kwok and Miller[8] proposed to discard completely from the right-side the contribution of the critical degrees of freedom, "since allowance for them leads to terms in F that differ from the Devonshire terms." The aforementioned terms correspond to the contribution made to F by the region of small k and are discussed below. However, as already noted, these corrections are proportional to the higher powers of $T\epsilon_{at}^{-1}$ and are small. In the principal approximation, on the other hand, an important contribution is made in the integrals (17) by the region of large k, and to determine this contribution it is necessary to put $\lambda_c = 0$ in the critical denominators, after which the critical degrees of freedom make contributions of the same order of magnitude to the constants as the remaining degrees of freedom.

4. GREEN'S FUNCTION. CORRELATION EFFECTS

The exact Green's function (12) satisfies Dyson's equations[15]

$$G_{ij}^{-1}(\mathbf{k}, i\omega_n) = (G_0^{-1}(\mathbf{k}, i\omega_n))_{ij} + \Sigma_{ij}(\mathbf{k}, i\omega_n), \tag{22}$$

where Σ_{ij} is the irreducible self-energy part. The graphic expansion of Σ in powers of the interaction, analogous to (15), can be written in the following form:



(23)

As noted above, the anharmonic effects are significant for the critical degrees of freedom in the region of small k. In addition, below the transition there appears in the crystal a piezoeffect, a linear coupling of the acoustic and optical branches proportional to the polarization, it being sufficient to take into account only the coupling with the critical branch. Thus, it is sufficient to determine the elements Σ_{cc} and Σ_{ac} of the matrix Σ_{ij} at small values of k, and the remaining Σ_{ij} can be neglected. Writing out the analytic expressions corresponding to the diagrams of (23), we get

$$\begin{aligned}\frac{v_c}{z_c^2}\Sigma_{cc}^{\alpha\beta}(0, i\omega_n) = {}& \delta_{\alpha\beta}\frac{Tv_c d_{11}(i\omega_n)}{2z_c^2} - 2q_{\alpha\beta\gamma\delta}u_{\gamma\delta} + 3(b_{11} + Te_{11}(i\omega_n))\cdot \\ & \sum_\sigma \delta_{\alpha\sigma}\delta_{\beta\sigma}P_\sigma^2 + (b_{12} + Te_{12}(i\omega_n))\sum_{\sigma'\neq\sigma}(\delta_{\alpha\sigma}\delta_{\beta\sigma}P_{\sigma'}^2 + \delta_{\alpha\sigma}\delta_{\beta\sigma'}P_\sigma P_{\sigma'}) \\ & + 5c_{111}\sum_\sigma \delta_{\alpha\sigma}\delta_{\beta\sigma}P_\sigma^4 + c_{112}\sum_{\sigma'\neq\sigma}(\delta_{\alpha\sigma}\delta_{\beta\sigma}P_{\sigma'}^4 + 4\delta_{\alpha\sigma}\delta_{\beta\sigma'}P_\sigma^3 P_{\sigma'}) \\ & + 2c_{123}\sum_{\sigma\neq\sigma'\neq\sigma''}(\delta_{\alpha\sigma}\delta_{\beta\sigma}P_{\sigma'}^2 P_{\sigma''}^2 + \delta_{\alpha\sigma}\delta_{\beta\sigma'}P_\sigma P_{\sigma'} P_{\sigma''}^2),\end{aligned} \tag{24}$$

$$\begin{aligned}\Sigma_{ac}^{\alpha_a\beta}(\mathbf{k}, i\omega_n) = Q_{\alpha\beta} = 2iz_c\Big[& q_{12}k_\alpha P_\beta + \frac{q_{44}}{2}(P_\alpha k_\beta + \delta_{\alpha\beta}(\mathbf{kP})) \\ & + q_a\sum_\sigma e_\sigma^\alpha e_\sigma^\beta(\mathbf{k}\mathbf{e}_\sigma)(\mathbf{P}\mathbf{e}_\sigma)\Big], \quad ka \ll 1.\end{aligned} \tag{25}$$

We use here the same notation as in (17) and (21); q_{ik}—coefficients of electrostriction, $q_a = q_{11} - q_{12} - q_{44}$—is the striction anisotropy constant. $d_{11}(i\omega_n)$ and $e_{\alpha\beta}(i\omega_n)$ in (24) differ from $d_{11} = d_{11}(0)$ and $e_{\alpha\beta} = e_{\alpha\beta}(0)$ in (17) and (21) because the diagrams d and h–n in (24) differ from f and i–l in (15). In (15), these diagrams contain the Green's function at the same value of the frequency $i\omega_n$ over which the sum is being taken. In the analogous diagrams of (23), one of the G contains besides the internal frequency ω_m also the external frequency ω_n: $G(k, i\omega_m) \rightarrow G(k, i\omega_m + i\omega_n)$. However, if we disregard the case of very low transition temperatures, on the order of several degrees, then at small values of k the thermodynamic contribution of the terms with $n \neq 0$ is much smaller than when $n = 0$, and the argument of d_{11} and $e_{\alpha\beta}$ can be omitted. A similar procedure can be used also in the analysis of the low-frequency dynamics, presented in Sec. 5, when $i\omega_n$ in (24) is replaced by the frequency ω: $d_{11}(\omega) \approx d_{11}$ and $e_{\alpha\beta}(\omega) \approx e_{\alpha\beta}$, since at the large values of k that are essential for the integrals (17) the frequency ω can be neglected together with other terms of the denominators G.

Taking (22), (24), and (25) into account, the Green's function assumes in place of (13) the form

$$G^{-1}(\mathbf{k}, i\omega_n) = \\ = \begin{pmatrix} \mathcal{M}\omega_n^2 + A & \omega_n^2\sqrt{\mu} + V + Q & \omega_n^2\sqrt{\mu_r} + V_r & 0 & 0 \\ \omega_n^2\sqrt{\mu} + V^+ + Q^+ & \omega_n^2 + S_0 + S & S_{cr} & i\mathbf{k}z_c & z_c\frac{\omega_n}{c} \\ \omega_n^2\sqrt{\mu_r} + V_r^+ & S_{rc} & \omega_n^2 + \lambda_r + S_{rr'} & i\mathbf{k}z_r & z_r\frac{\omega_n}{c} \\ 0 & -i\mathbf{k}z_c & -i\mathbf{k}z_r & -\frac{v_c}{4\pi}k^2 & 0 \\ 0 & -z_c\frac{\omega_n}{c} & -z_r\frac{\omega_n}{c} & 0 & \frac{v_c}{4\pi}\left(\frac{\omega_n^2}{c^2} + k^2\right) \end{pmatrix}. \tag{26}$$

Here $S_0 = \Sigma_{cc} + \lambda_c$, the second row and column correspond to the critical coordinates x_c, the third to x_r, and to abbreviate the notation the index c has been omitted from the critical matrices V, S, and $\sqrt{\mu}$.

It will be shown in Sec. 5, that the elements of the matrix $(S_0)_{\alpha\beta}$ at $\mathbf{k} = 0$ and $\omega_n = 0$ can be simply expressed in terms of the dielectric-constant matrix $\epsilon_{\alpha\beta}$ of a clamped crystal. Therefore formula (24) can be obtained also by a purely thermodynamic method with the aid of relations (38), (20), and (21).

We shall now discuss the correlation effects[3,14], i.e., the additional terms that result from substituting in the right-sides of (15) and (17) for F and (23) for Σ the exact Green's function in place of the previously employed G^{00}, corresponding to (26) with $F_0 = Q = 0$. Let us find, for example, the correction $\delta\Sigma$ to the diagrams c of (23) for Σ at $\mathbf{k} = \omega_n = 0$. For simplicity we confine ourselves to the region above the transition temperature T_0 and to the case of not too small T_0. With this, as already mentioned, it is sufficient to retain only the classical term with $n = 0$ in the sum over the frequencies ω_n, corresponding to the internal line of the diagram:

$$\delta\Sigma_{\alpha\beta}^{(2c)}(0,0) = 3T\sum_{\mathbf{k},\,ij} V_{\alpha\beta ij}^{00\mathbf{k}-\mathbf{k}}\left(G_{ij}(\mathbf{k},0) - G_{ij}{}^{00}(\mathbf{k},0)\right). \tag{27}$$

For the function G in (27), in accordance with the successive-approximation method, we take expression (25), and at the considered $T > T_0$ we have $S_0 = 4\pi\lambda\epsilon_0^{-1}$ and $\epsilon_0 = C_+(T - T_c)^{-1}$. The integral (27) converges at small $k \sim a^{-1}\epsilon^{-1/2}$, so that (27) contains the values of G and G^{00} for small k. With this, the matrices V_b and $S_{bb'}$ (8), which describe the intertwining of the different branches, tend to zero in accordance with (9). It is therefore sufficient to take into account in G only the critical and acoustic branches, for which the denominators of the Green's functions are small at small values of k, and in formula (27) it is sufficient to retain only the critical components G_{cc}, inasmuch as the acoustic potentials $V_{\alpha\beta\gamma\delta_a}^{ook-k}$ and $V_{\alpha\beta\gamma_a\delta_a}^{ook-k}$ vanish at small values of $\mathbf{k}$ as a result of (2). After eliminating the electromagnetic and acoustic components, G_{cc} takes on the following form:

$$G_{cc} = (S_0 + S + \lambda g^l - V^+A^{-1}V)^{-1}, \tag{28}$$

where λ and g^i are the same as in (21) and (10). We see that the long-range dipole interaction produced in (28) a longitudinal term proportional to g^i, with a coefficient λ of the order of the square of the plasma frequency of the ions and much larger at the considered small values of k than the remaining terms of the denominator in (28). Therefore the longitudinal degree of freedom in the region $a^{-1} \gg k \gg L^{-1}$ under consideration ceases to be critical[7,10,4] and it is sufficient to take into account in (27) only the transverse components:

$$\delta\Sigma_{\alpha\beta}^{(2c)} = 3T\sum_{\mathbf{k}} V_{\alpha\beta\gamma\delta}^{0000}\left[(S_0 + S - V^+A^{-1}V)_t^{-1} - (S - V^+A^{-1}V)_t^{-1}\right]. \tag{29}$$

The indices $(\ldots)_t^{-1}$ of the matrix R denote here that R must be projected on a subspace (plane) orthogonal to $\mathbf{n}$, $R_t = g^tRg^t$, after which it is necessary to take in this subspace the matrix inverse to R_t. The values of the elements of R_t^{-1} can be obtained from the matrix $(R + \lambda g^l)^{-1}$, by letting $\lambda \to \infty$;

$$(R_t^{-1})_{\alpha\beta} = \left(\sum_{\mu\nu} n_\mu n_\nu A_{\mu\nu}(0)\right)^{-1}\frac{\partial}{\partial\xi}A_{\alpha\beta}(\xi)\,|_{\xi=0}, \tag{30}$$

where $A_{\alpha\beta}(\xi)$ is the cofactor of the matrix element $R_{\alpha\beta} + \xi n_\alpha n_\beta$.

Substituting in (29) the expressions (9) for S, V, and A, and introducing in the integration with respect to k a new variable $x = |k|\,\epsilon_0^{1/2}\lambda^{-1/2}$, the integral (29), with allowance for the cubic symmetry, can be transformed into

$$\delta\Sigma_{\alpha\beta}^{(2c)} = -\delta_{\alpha\beta}4\pi\lambda T\varepsilon_0^{-1/2}J_{2c}, \tag{31}$$

where

$$J_{2c} = \frac{3}{2^6\pi^5}\lambda^{3/2}(b_{11} + 2b_{12})\int_0^\infty dx\int d\mathbf{n}\,\mathrm{Sp}\left[(1 + x^2\varphi)_t^{-1}\varphi_t^{-1}\right],$$

$$\varphi = s_tg^t + s_ag^a - (v_tg^l + v_ag^a)(a_lg^l + a_tg^t + a_ag^a)^{-1}(v_tg^t + v_ag^a), \tag{32}$$

g^i and $b_{\alpha\beta}$ are the same as in (10) and (20), and $d\mathbf{n}$ denotes integrations over the angles of the vector $\mathbf{n}$.

The correction to the diagram d of (23) is calculated in similar fashion. The answer has likewise the form (31), and the corresponding constant J_{2d} is proportional to quadratic combinations of the striction constants q_{ik} divided by the elastic moduli c_{ik}. Owing to the already mentioned relative smallness of $b_{\alpha\beta}$, it is necessary in the quantitative calculation to take into account also certain diagrams omitted from (23), i.e., the diagrams f–n, in which two dashed lines are replaced by one solid line. The contribution of these terms reduces to the substitution $b_{\alpha\beta} \to Th_{\alpha\beta}$ in (32), where $h_{\alpha\beta} \sim e_{\alpha\beta}$ in (20).

The quantities $\lambda^{-1}(G_{cc}^{-1})_{\alpha\beta}$ at $\mathbf{k} = \omega_n = 0$, in accordance with the formula (38) given below, form a matrix which is the inverse of the dielectric constant matrix $\epsilon_{\alpha\beta}$. Therefore the formula for ϵ with first-approximation corrections is

$$\varepsilon = \left(\frac{1}{\varepsilon_0} - \frac{JT}{\sqrt{\varepsilon_0}}\right)^{-1} \simeq \frac{C_+}{T - T_c}\left(1 + JT\sqrt{\frac{C_+}{T - T_c}}\right), \tag{33}$$

where J is equal to the sum of the already mentioned terms given in (32).

The correction term in (33) has the usual form characteristic of corrections to the zeroth approximation of the self-consistent field[14,3].. An analogous form is possessed by the correction terms for the other thermodynamic quantities[3]. The constant J is equal in order of magnitude to the reciprocal of the atomic energy ϵ_{at}^{-1}; therefore, as already noted, the fundamental parameter determining the suitability of the zeroth approximation (20) and (26) and the smallness of the correlation effects is $T\epsilon_{at}^{-1}$.

Let us estimate the correction term in (33) for $BaTiO_3$. In this substance $b_{\alpha\beta}$, $Te_{\alpha\beta}$, and $q_{ik}^2c_{ik}^{-1}$ are quantities of the same order of magnitude, so that formula (32) can be used for the estimate of J. The quantity λ enters into the formulas for the spectrum of the critical vibrations (41), and from a comparison with the data of[17] it can be concluded that $\lambda^{1/2} \sim 10^{13}$ Hz. We have no data concerning s_i and v_i in $BaTiO_3$, but for $SrTiO_3$ we have $s_i \sim a_i$[18], so that we can expect the same to hold here, too. Using for $b_{\alpha\beta}$ and a_i the values given in[1], we get

$$J \sim \frac{3}{32\pi^3}\,\frac{\lambda^{3/2}(b_{11} + 2b_{12})}{s_t^{3/2}} \sim \frac{1}{70\ \mathrm{eV}}, \qquad JT \sim 5\cdot 10^{-4}. \tag{34}$$

At the transition point, the correction term $JT\sqrt{\epsilon_0}$ in (33) amounts to ~5%.

5. VIBRATION SPECTRUM AT SMALL VALUES OF k

The dynamic properties of the system are best described with the aid of the time-dependent Green's function[15] $G^{(t)}$:

$$G_{ij}^{(t)}(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = \langle \hat{T}(\xi_i(\mathbf{r}_1, t_1) - \overline{\xi}_i)(\xi_j(\mathbf{r}_2, t_2) - \overline{\xi}_j)\rangle,$$
$$\xi_i(t) = e^{iHt}\xi_i e^{-iHt}. \tag{35}$$

The Fourier component of the time-dependent function $G^{(t)}(k, \omega)$ can be obtained from the temperature function $G(k, i\omega_n)$ (12) with the aid of an analytic continuation from the discrete set of points $i\omega_n$ in the complex ω plane to the real axis[15]:

$$G^{(t)}(\mathbf{k}, \omega) = G(\mathbf{k}, \omega). \tag{36}$$

Thus, in the approximation in question $G^{(t)}$ is the matrix (26) with the substitution $\omega_n \rightarrow -i\omega$.

The excitation spectrum is determined by the poles of $G^{(t)}$, i.e., by the values of the frequencies at which the corresponding system of homogeneous equations has a solution[15]; in this case the eigenvectors ξ_i determine the amplitudes of the displacements in the excitation. Going over for the sake of clarity from components of the potential to the electric field **E**, we have for the determination of the spectrum the following equations:

$$\begin{gathered}(A - \mathscr{M}\omega^2)\mathbf{u} + (V + Q - \omega^2\sqrt{\mu})\mathbf{x}_c + (V - \omega^2\sqrt{\mu_r})\mathbf{x}_r = 0,\\ (V^+ + Q^+ - \omega^2\sqrt{\mu})\mathbf{u} + (S_0 + S - \omega^2)\mathbf{x}_c + S_{cr}\mathbf{x}_r - z_c\mathbf{E} = 0,\\ (V_r{}^+ - \omega^2\sqrt{\mu_r})\mathbf{u} + S_{rc}{}^+\mathbf{x}_c + [(\lambda_r - \omega^2)\delta_{rr'} + S_{rr'}]\mathbf{x}_{r'} - z_r\mathbf{E} = 0,\\ \frac{4\pi\omega^2}{c^2 v_c}(z_c\mathbf{x}_c + z_r\mathbf{x}_r)_\alpha + \left(\frac{\omega^2}{c^2}\delta_{\alpha\beta} - k^2\delta_{\alpha\beta} + k_\alpha k_\beta\right)E_\beta = 0.\end{gathered} \tag{37}$$

The system (37) differs from the ordinary equations of harmonic oscillations in that the quantities S_i and Q have a temperature and deformation dependence. These equations are quite lucid, and analogous semi-phenomenonological relations were written out earlier by Ginzburg[9,14] and Cochran[10,11], and called by then "linear anharmonic approximation." These equations were derived above microscopically, and the regular method employed makes it possible to investigate also higher approximations in the parameter $T\epsilon_{at}^{-1}$, particularly damping effects[4].

At small values of k and ω, the coupling between the critical or the acoustic branch and the other branches in (37) is small, the components x_r can be neglected, and the expansions (9) and (25) can be used for A, V, S, and Q.

In the case when macroscopic wavelengths larger than or of the same order as the crystal dimension L are considered, the vector k in (37) should be replaced by the differentiation operator $\partial/\partial\mathbf{R}$, and (37) goes over into the equations of elasticity and electrodynamic theory[19], with allowance for the piezoeffect below T_0. It is seen from (37) that when oscillations in a homogeneous field E are considered the piezoelectric coupling between the critical branch, which determines the polarization, and the acoustic branch will be noticeable only for frequencies $\omega \lesssim L^{-1}a_i^{-1/2}$, i.e., in the region of the piezoacoustic resonances. At larger frequencies, the coupling between the branches decreases like ω^{-2}, so that the quantity S_0 in (37) determines the dielectric constant ϵ at these high frequencies, called the permittivity of the clamped crystal:

$$\varepsilon_{\alpha\beta} = \lambda(S_0{}^{-1})_{\alpha\beta}, \qquad S_0 = \lambda/\varepsilon. \tag{38}$$

After eliminating from (37) the components of **E**, the equations for the spectrum at small values of k and ω become

$$\begin{gathered}(A - \mathscr{M}\omega^2)\mathbf{u} + (V + Q - \omega^2\sqrt{\mu})\mathbf{x}_c = 0,\\ (V + Q^+ - \omega^2\sqrt{\mu})\mathbf{u} + \left(\frac{\lambda}{\varepsilon} + S - \omega^2 + \lambda g^l - \lambda g^t\frac{\omega^2}{c^2k^2 - \omega^2}\right)\mathbf{x}_c = 0.\end{gathered} \tag{39}$$

If we disregard very long wavelengths, $k^{-1} \gtrsim 10^{-3}$ cm, where the well-known entanglement of the phonon and electromagnetic branches takes place[20,4], then the relativistic transverse term in (39) can be neglected. One of the six remaining branches, the longitudinal optical branch, has a high frequency $\omega \sim \lambda^{1/2}$, and will not be considered here, inasmuch as on going from (37) to (39) we have assumed that the frequencies were low. There remain therefore in (39) only the transverse critical coordinates, and the equation for the spectrum can be written in the form

$$\begin{gathered}\mathrm{Det}\|A - \mathscr{M}\omega^2 - (V + Q - \omega^2\sqrt{\mu})(\lambda/\varepsilon + S - \omega^2)_t{}^{-1}\cdot\\ \cdot(V + Q^+ - \omega^2\sqrt{\mu})\| = 0,\end{gathered} \tag{40}$$

where the symbol $(\ldots)_t^{-1}$ is the same as in (29) and (30).

Owing to the transversality of the critical matrix, the longitudinal parts of the matrices S, V, and Q make no contribution to (40). We can therefore discard the term proportional to k_β in the matrix $Q_{\alpha\beta}$ (25), and in the matrices V and S (9) we can put $v_l = v_t$ and $s_l = s_t$, after which V and S become diagonal relative to the principal axes of the crystal. If the elastic, striction, and dielectric constants are known, the spectrum of the five branches given by (40) is determined by six constants, namely λ, μ, s_t, s_a, v_t, and v_a, which can be determined experimentally. We note, however, that since it is possible to choose as the acoustic coordinate in Sec. 2 the coordinate of any of the ions of the cell, the determination of these constants from the spectrum is not completely unique. The oscillation frequencies are expressed only in terms of such combinations of λ, μ, s_i, and v_i which do not depend on the indicated choice; therefore a complete spectrum experiment can determine only several possible sets of constants (as many as there are nonequivalent atoms in the cell).

The five branches described by Eqs. (40) break up at the smallest values of k into three acoustic branches with a linear dependence of ω on k, and two transverse critical branches with a gap in the spectrum proportional to $\epsilon^{1/2} \sim |T - T_c|^{1/2}$. Thus, in the tetragonal phase we have

$$\omega_{c1}{}^2(0) = \frac{\lambda}{(1 - \mu/M)\varepsilon_\perp}, \qquad \omega_{c2}{}^2(0) = \frac{\lambda}{1 - \mu/M}\left(\frac{n_1{}^2}{\varepsilon_\perp} + \frac{n_\perp{}^2}{\varepsilon_\parallel}\right). \tag{41}$$

Besides the temperature dependence of the gap, an essential singularity of the spectrum is that it varies strongly at wavelengths much larger than the interatomic distances a. Thus, in the region $a^{-1} \gg k \gg a_i^{-1/2}\omega_c(0)$ it is possible to neglect S_0 and Q in (40), and all five branches have a linear dependence of ω on k. When $k \sim a_i^{-1/2}\omega_c(0)$, a strong kink occurs in the dependence of the acoustic frequencies on k, and the speeds of sound at small and large frequencies are not equal (see the figure).

By way of illustration let us consider particular cases in (40). If k is directed along x, then the five branches of (40) break up into one longitudinal acoustic

branch and two pairs of degenerate transverse oscillations. On the other hand, if k is perpendicular to the tetragonal axis and directed along one of the principal axes or makes an angle 45° with it, then only one pair of branches, with a polarization perpendicular to k and to **P**, is separated, while the remaining transverse branches are coupled below T_0 with the longitudinal branch, the dispersion equations being cubic:

1) $n_1 = 1, \quad n_2 = n_3 = 0$:

$$\omega_l^2 = k^2(a_l + a_a),$$

$$(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda}{\varepsilon_\perp}\right) - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2 - \frac{\lambda P^2 q_{44}^2}{4\pi\rho}k^2 = 0; \tag{42a}$$

2) $n_2 = 1, \quad n_1 = n_3 = 0$:

$$(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda}{\varepsilon_\perp}\right) - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2 = 0,$$

$$[k^2(a_l + a_a) - \omega^2]\left[(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda}{\varepsilon_\parallel}\right) - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2\right]$$
$$- (k^2a_t - \omega^2)\frac{\lambda P^2 q_{12}^2}{\pi\rho}k^2 = 0; \tag{42b}$$

3) $n_1 = 0, \quad n_2^2 = n_3^2 = {}^1/_2$:

$$\left[k^2\left(a_t + \frac{a_a}{2}\right) - \omega^2\right]\left[k^2\left(s_t + \frac{s_a}{2}\right) - \omega^2 + \frac{\lambda}{\varepsilon_\perp}\right]$$
$$- \left[k^2\left(v_t + \frac{v_a}{2}\right) - \omega^2\sqrt{\frac{\mu}{M}}\right]^2 = 0,$$

$$\left[k^2\left(a_l + \frac{a_a}{2}\right) - \omega^2\right]\left[(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda}{\varepsilon_\parallel}\right)\right.$$
$$\left. - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2\right] - (k^2a_l - \omega^2)\frac{\lambda P^2 q_{12}^2}{\pi\rho}k^2 = 0. \tag{42c}$$

To illustrate the angular dependence of the spectra below T_0, let us consider also a hypothetical case of a crystal in which the constants introduced in (9) are $a_a = v_a = s_a = 0$. Although in $BaTiO_3$, for example, the elastic anisotropic constant a_a is of the same order as a and a_l, this anisotropy is usually small in the observable quantities. It is more convenient in this case to perform the calculations in a coordinate system in which one of the axis is directed along **k**, the other is perpendicular to **k** and **P**. Here, again, a pair of branches with polarization perpendicular to **k** and **P** is separated, and for the remaining branches we obtain a third-degree equation

$$(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda}{\varepsilon_\perp}\right) - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2$$
$$- \frac{\lambda P^2 k^2 n_1^2}{\pi\rho}\left(\frac{q_{44}}{2} + q_a n_\perp^2\right)^2 = 0,$$
$$(k^2a_l - \omega^2)\left[(k^2a_t - \omega^2)\left(k^2s_t - \omega^2 + \frac{\lambda n_\perp^2}{\varepsilon_\parallel} + \frac{\lambda n_1^2}{\varepsilon_\perp}\right)\right.$$
$$\left. - \left(k^2v_t - \omega^2\sqrt{\frac{\mu}{M}}\right)^2\right] - \frac{\lambda P^2 k^2}{\pi\rho}\left[(k^2a_l - \omega^2)n_1^2\left(\frac{q_{44}}{2} + q_a n_\perp^2\right)^2\right.$$
$$\left. + (k^2a_t - \omega^2)n_\perp^2(q_{12} + q_a n_1^2)^2\right] = 0. \tag{43}$$

In $BaTiO_3$, $\epsilon_\perp$ is much larger than $\epsilon_\parallel$, and q_a is much larger than the constants q_{12} and $q_{44}/2$, so that the anisotropy of the spectrum below T_0 is appreciable.

The formulas of this section were obtained by neglecting relaxation processes. In particular, they correspond to isothermal oscillations, whereas the oscillations can be also adiabatic, depending on the ratios of k and ω, on the one hand, to the coefficients of thermal conductivity and viscosity on the other[1]. However, these effects are proportional to higher powers of $T\epsilon_{at}^{-1}$ and are small. For example, in $BaTiO_3$ the difference between the adiabatic dielectric constant and the isothermal one is ~3%[1]. The damping of the oscillations[17] and the dielectric losses at microwave frequencies will be considered in a separate paper.

6. CONCLUSION

In conclusion, we make two remarks, one concerning the method and the other concerning the experiment.

Let us discuss the connection between the present work and the description of the transition by the self-consistent field method[3,4]. In[3,4], the radius r_0 of the interaction of ions of different cells was assumed to be large. Therefore the interaction was accurately described by means of the average self-consistent field, and the correlation effects were proportional to r_0^{-3}. In the present paper, the small parameters are the anharmonicity $T\epsilon_{at}^{-1}$ and the anomalously small rigidity $\lambda_c \sim \lambda_r T\epsilon_{at}^{-1}$. The unharmonic correlation effects are significant only for phonons with small $k \sim a^{-1}T^{1/2}\epsilon_{at}^{-1/2}$, and the motion of the remaining phonons can be regarded as harmonic and independent of the transition. Therefore, in the calculation of the field acting on a given ion, the main contribution is made by the noncritical phonons, and the field can be regarded as independent of the position of the ion and replaced by the mean value, neglecting correlations.

Thus, the approximation employed is similar to the approximation of the self-consistent field, except that in[3,4] they used the smallness of the correlation of the particles in different cells, whereas here, at small anharmonicity, the phonons with different k are independent of one another. Therefore the general results and the form of the temperature dependences (20), (33), (41) remain the same as in[3,4] and in the phenomenological theories[16,19,14,10]. Only the expression for the phenomenological constants in terms of the microscopic parameters changes: in[3,4] they were expressed in terms of the average temperature constants for the independent particles, but in our case they are expressed in terms of the averages for the independent phonons. This explains why the results obtained in the models of Devonshire[16] and Slater[6], who used the self-consistent field method, coincide with the results obtained in the case of weak anharmonicity[7] and with experiment. In this connection, the idea advanced in[4], that the success of the phenomenological theory for perovskites indicates that the r_0 of these systems is large, does not necessarily follow; a sufficient and more probable explanation is the smallness of λ_c and the weak anharmonicity.

Physically, the applicability of the method of the self-consistent field differs from that of the expansion in the anharmonicity. For the former it is necessary to have a large radius r_0, but the anharmonicity can be arbitrarily large, particularly, this may be the case of the order-disorder transition[3,4]. The regions of applicability can, of course, also overlap; for example, at large r_0 the quantity s_t in (34) is proportional to r_0^2 and the correlation correction is proportional to r_0^{-3}.

The second remark pertains to the structure of the crystals in question. As already noted, in perovskites the constants $e_{\alpha\beta}$ and $c_{\alpha\beta\gamma}$ in (20) are anomalously large compared with the first-approximation constant $b_{\alpha\beta}$, causing, in particular, the closeness of the first-order transition to the second-order transition. In accordance with (21) and (17), this denotes that the critical potentials $V^{(6)}$ are much larger, in the appropriate atomic units, then the potentials $V^{(4)}$. Large values of $V^{(6)}$ may be connected with the well-known singularity of these structures—the close packing with very small "free space" for relative displacements of the ions[1]. This can lead to a sharp growth of the repulsion at values of x_c that are not small, i.e., to a situation of the square-well type. In this connection, great interest attaches to a determination of the microscopic potential $V^{(n)}$ in (21), i.e., the constant z_c or λ, which, as discussed in Sec. 5, can be accomplished by studying the dynamics. It is also very desirable to search for transitions of the displacement type in other non-ferroelectric and non-oxygen-octahedral crystals, since it is clear from the foregoing that the singularities of the thermodynamics and dynamics of the displacement-type transition are not at all connected with ferroelectricity and may have a general character.

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