SOLID MATTER

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ROLE OF FLUCTUATIONS IN THE COHERENT DISPLACEMENTS OF ATOMIC EQUILIBRIUM POSITIONS AT SECOND-ORDER PHASE TRANSITIONS

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Second-order phase transitions in ferroics of the ferroelastic type have been studied theoretically. The temperature-induced phase transition in crystals with a wide forbidden gap caused by the interaction between electrons and a branch of acoustic vibrations in the crystal lattice is considered. The vertex part of this interaction with transverse lattice vibrations is calculated. The characteristic features of the thermodynamic potential at the transition point and the temperature dependence of the acoustic phonon dispersion at the transition over quasiequilibrium states are discussed. It is shown that the stabilization of structure fluctuations by the electron subsystem in the high-symmetry phase, and a reduction of soft mode frequencies makes those fluctuations metastable.

K e y w o r d s: thermodynamic potential, structure transformation, electron-phonon interaction, oscillation mode, wave function, deformation, Hamiltonian, Green function.

1. Introduction

The idea of the thermodynamic equivalence of a crystal and a system of quantized fields of its elementary excitations (quasiparticles) [1] allows the methods of quantum field theory to be successfully used in theoretical researches dealing with structural phase transitions in crystals. According to work [2], if the properties of elementary excitations and the interactions that exist between them are determined experimentally at a certain temperature, the equations of motion of quantized fields make it possible to determine those properties at any other temperature. This way can be used to determine the structure and the properties of a crystal itself. The method of temperature (Matsubara) Green's functions allows one to solve such a problem with regard for both quantum and thermal fluctuations. In the framework of this method, a modification of the crystal structure at

structural transformations of the displacement type is determined as coherent deviations of normal coordinates for some phonon-field modes from their previous values.

A second-order phase transition (PT2) of the displacement type occurs owing to coherent displacements of equilibrium atomic positions in the crystal along the normal coordinate of one of the vibration modes in this crystal. Therefore, such a transition may take place as a result of the interaction between a certain branch in the spectrum of crystal vibrations that corresponds to the selected mode and the electron subsystem of the crystal. The state of the electron subsystem also depends on the distribution of atoms, as well as on the electron density, in a unit cell of the crystal. It is clear that if this mode belongs to the branch of transverse dipole vibrations in the crystal, the latter, after the transition, may become a medium with dipole polarization. In this case, we speak about the ferroelectric PT2. If the active mode belongs to a branch of transverse acoustic vi-

brations, PT2 is of the ferroelastic type. At last, if the active mode belongs, e.g., to a branch of oscillations of atomic magnetic moments in the crystal, the transition makes the crystal ferromagnetic or, in the general case, multiferroic.

For the discussed structural transformations to be stable, it is necessary that the displacements of atoms be energetically beneficial. This can be realized only if the electron density in a crystal unit cell undergoes a redistribution. Below, we demonstrate that such a redistribution takes place if the displacements of atoms along the active normal coordinate mix the wave functions of valence electron states with the wave functions of electron states in the conduction band. The electron-phonon interaction must be interband at that.

We determined conditions that make PT2 of any displacement type possible and the properties of those transitions. In particular, we succeeded in determining the peculiarities in the temperature dependence of the thermodynamic potential at the PT2 point [3], the existence of which was pointed out by L.D. Landau and E.M. Lifshitz [4]. In work [3], we showed that the peculiarity is a logarithmic divergence and, hence, cannot be expressed in terms of power-law functions, as it is done in the theory of critical exponents [5].

The theory of ferroelectric PT2 demonstrates an important role of transverse polarization crystal vibrations. According to work [6], this theory is based on the observed spontaneous emergence of a crystal polarization as the temperature T decreases and on the tending of the crystal dielectric permittivity ϵ to infinity, when approaching the phase transition temperature $T = T_c$. The Lyddane–Sachs–Teller relation $\epsilon_0/\epsilon_\infty = \omega_{||}^2/\omega_\perp^2$ [7] enables this structural transition to be associated with the tending of the transverse polarization wave frequency $\omega_\perp$ to zero (the so-called soft mode). Two mechanisms of soft mode emergence as a result of the electron–phonon interaction are known. One of them is suitable for the description of PT2 in crystals with a narrow energy gap, when the driving force of the transition consists in a variation of the conduction band occupation by charge carriers as the temperature changes [3,4]. The other interband mechanism [8] successfully describes PT2 in crystals with a wide energy gap, when the driving force is no more than the mixing of electron states in the valence and conduction bands under the influence of virtual interband electron transitions accom-

panied by the emission and the absorption of transverse phonons. The important role of just transverse vibrations of the crystal lattice in the structural PT2 is evident. It is so, because for any superposition of transverse vibrations, the divergence of displacements turns out equal to zero. This means that such superpositions do not break the translational symmetry of the crystal (if the domain effects are neglected). At the same time, the divergence of displacements differs from zero for longitudinal vibrations. Therefore, the latter are capable, e.g., of localizing the charge carriers in the conduction band [9, 10], thus violating the translational symmetry of the crystal. Below, we consider possible structural modifications under the influence of the interaction between the electrons and the transverse acoustic vibrations in crystals with a wide energy gap ΔE, which considerably (by several orders of magnitude) exceeds the acoustic vibration quantum energy.

2. Hamiltonian of Interband Interaction between Charge Carriers and Transverse Acoustic Vibrations

A similar model of interband electron–phonon interaction, which can generate a ferroelectric PT2, was considered by us earlier in work [3] with the use of an interaction operator found and tested in a number of works carried out by a group of Leningrad scientists. A review of those works was made in monograph [8]. The scientific literature contains numerous descriptions for the operator of interaction between charge carriers and longitudinal acoustic phonons. Unfortunately, every description is accompanied by a remark that this operator is not suitable for the consideration of the interaction with transverse phonons. Therefore, our first task consists in the construction of the corresponding Hamiltonian.

Let $W_0(\mathbf{r})$ be the potential energy of an electron as a function of its radius-vector $\mathbf{r}$ in the high-temperature (high-symmetry) phase, when the crystal atoms (ions) are located at their equilibrium positions. Then, the function $W_0(\mathbf{r})$ is periodic with the crystal lattice period. Of course, the displacements of atoms in the crystal lattice change the electron energy. We should consider those changes in the case where the displacements correspond to a propagating transverse acoustic wave. In the transverse wave with wave vector $\mathbf{q}$, the crystal unit cells become shifted as

a whole (undergoing no deformation) in the direction perpendicular to **q**. Such purely transverse waves, as well as purely longitudinal ones, occur very seldom in crystals. For instance, in a cubic crystal, the purely transverse and purely longitudinal waves can propagate only along three basic lattice axes. Nevertheless, the cubic crystal is often simulated by an isotropic medium, in which similar waves do exist for any wave-vector direction. In this model, the deformations of an internal crystal structure and a unit cell shape, which arise at the propagation of transverse acoustic waves, are neglected. We shall also neglect those deformations. If a transverse acoustic wave propagates along the wave vector **q** and two neighbor unit cells shift at that along the plane of their contact without deformation, the variation of the electron energy in either of the cells will be determined by the gradients of the function $W_0(\mathbf{r})$. In addition, another crucial quantity is the difference between the displacement magnitudes of the centers of the n-th and $(n+1)$-th cells.

Making no allowance for the interaction, the Hamiltonian for an electron in the crystal looks like

$$H_0 = -\frac{\hbar^2}{2m}\nabla_z^2 + W_0(\mathbf{r}). \tag{1}$$

Its eigenfunctions are the Bloch functions

$$\psi_{k\sigma}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_n \exp(i\mathbf{k}\mathbf{r})\phi_\sigma(\mathbf{n}+\boldsymbol{\rho}),\ \mathbf{r}=\mathbf{n}+\boldsymbol{\rho}, \tag{2}$$

where σ is the index of the electron energy band, **n** the crystal lattice vector, $\phi_\sigma(\mathbf{n}+\boldsymbol{\rho})$ a periodic (with the lattice period) wave function of the electron radius-vector $\boldsymbol{\rho}$ in the n-th unit cell. For any **n,** the function ϕ_σ has the same dependence on $\boldsymbol{\rho}$. Every eigenfunction $\psi_{k\sigma}(\mathbf{r})$ is related to the electron energy $E_\sigma(\mathbf{k})$. In the model where only two bands, the valence ($\sigma = 1$) and conduction ($\sigma = 2$) ones, are present, and one branch of transverse acoustic phonons are taken into consideration, the system of noninteracting electrons and crystal phonons is described by the following Hamiltonian written down in the secondary quantization representation (hereafter, the system of units with $\hbar = 1$ and the Boltzmann constant $k = 1$ is used):

$$H_0 = \sum_{\mathbf{k},\sigma=1}^{2} E_\sigma(\mathbf{k})a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} + \sum_{\mathbf{q}} \omega(\mathbf{q})b_{\mathbf{q}}^+ b_{\mathbf{q}}. \tag{3}$$

In expression (3), $a_{\mathbf{k}\sigma}^+$ and $a_{\mathbf{k}\sigma}$ are the operators of electron creation and annihilation, respectively, in the state with the Bloch wave function $\psi_{k\sigma}(\mathbf{r})$; and $b_{\mathbf{q}}^+$ and $b_{\mathbf{q}}$ are the creation and annihilation, respectively, operators for the transverse acoustic phonon with the momentum **q** and the energy $\omega(\mathbf{q})$.

Now, let us construct a Hamiltonian for the interaction between electrons and a branch of transverse acoustic vibrations, the displacement vectors of which lie in the contact plane of two adjacent cells, and the wave vector **q** can be arbitrary. For every given vector **q**, the vector $\mathbf{u_n}$ describing the displacement of the **n**-th cell center and oriented perpendicularly to the vector **q** is selected from those that lie in the indicated plane. The displacement magnitude can be presented with the use of the operators $b_{\mathbf{q}}^+$ and $b_{\mathbf{q}}$ as follows:

$$u_n = \sum_{\mathbf{q}} \sqrt{\frac{1}{2MN\omega_0(\mathbf{q})}} \exp\left[i(\mathbf{qn})\right]\left(b_{\mathbf{q}}+b_{\mathbf{q}}^+\right), \tag{4}$$

where N is the number of cells in the crystal, and M the effective vibration mass. The displacement of the adjacent cell,

$$u_{n+1} = \sum_{\mathbf{q}} \sqrt{\frac{1}{2MN\omega_0(\mathbf{q})}} \exp\left[i(\mathbf{qn}+qa)\right]\left(b_{\mathbf{q}}+b_{\mathbf{q}}^+\right) \tag{5}$$

differs from the previous expression by the term qa in the exponent, where a is the crystal cell size measured along the vector **q**. By the order of magnitude, the quantity a can be regarded equal to the lattice constant. The interaction Hamiltonian should include the difference

$$\Delta u = u_{n+1} - u_n \approx$$
$$\approx \sum_{\mathbf{q}} \sqrt{\frac{1}{2MN\omega_0(\mathbf{q})}}\left(b_{\mathbf{q}}+b_{\mathbf{q}}^+\right)\exp(i\mathbf{qn})iqa, \tag{6}$$

multiplied by the gradient function $dW_0(\mathbf{r})/dx \equiv$ $\equiv f(\mathbf{r})$ determined in the cell, where the variable x changes along the direction of cell displacements in the considered acoustic wave. Hence, the Hamiltonian of the interaction between the systems of valence and conduction electrons, on the one hand, and phonons of one branch of transverse acoustic

phonons, on the other hand, has the following form in the secondary quantization representation:

$$H_i = \int d\boldsymbol{\rho} f(\boldsymbol{\rho}) \Psi^+(\boldsymbol{\rho}) \Psi(\boldsymbol{\rho}) \Delta u_n, \qquad (7)$$

where the operators Ψ are constructed with the use of the Bloch functions,

$$\Psi(\boldsymbol{\rho}) = \sum_{\mathbf{k}\sigma\mathbf{n}} a_{\mathbf{k}\sigma} \exp(i\mathbf{k}\mathbf{n}) \phi_\sigma(\mathbf{n} + \boldsymbol{\rho}),$$

$$\Psi^+(\boldsymbol{\rho}) = \sum_{\mathbf{k}'\sigma'\mathbf{n}'} a_{\mathbf{k}\sigma}^+ \exp(-i\mathbf{k}'\mathbf{n}') \phi_\sigma^+(\mathbf{n} + \boldsymbol{\rho}). \qquad (8)$$

Taking into account that

$$\int d\boldsymbol{\rho} \, \mathbf{g}(\boldsymbol{\rho}) \phi_\sigma^+(\mathbf{n} + \boldsymbol{\rho}) \phi_{\sigma'}(\mathbf{n}' + \boldsymbol{\rho}) = \mathbf{g}_{\sigma\sigma'}' \delta_{\mathbf{n}\mathbf{n}'}, \qquad (9)$$

we obtain

$$H_i = N^{-1/2} \sum_{\mathbf{k}\mathbf{q}\sigma\sigma'} F_{\sigma\sigma'}(\mathbf{k}, \mathbf{q}) a_{\mathbf{k}+\mathbf{q}\sigma'}^+ a_{\mathbf{k}\sigma} \left(b_{\mathbf{q}} + b_{-\mathbf{q}}^+ \right), (10)$$

where $F_{\sigma\sigma'}(\mathbf{k}, \mathbf{q}) = \frac{iqa}{\omega_0(\mathbf{q})} \sqrt{\frac{\omega_0(\mathbf{q})}{2M}} \mathbf{g}_{\sigma\sigma'}'$, and the subscripts σ and σ' equal 1 and 2. For acoustic waves, the quantity $q/\omega_0(\mathbf{q})$ equals the reciprocal phase velocity of a transverse wave, v^{-1}, which is constant in a wide interval of wave vectors, except for the values $q \approx \pi/a$. A crucial role is played by the dependence of the quantity $\sqrt{\omega_0(\mathbf{q})}$ on $\mathbf{q}$. A similar dependence of the vertex part F on $\mathbf{q}$ was also found for longitudinal acoustic phonons [7].

To analyze the described model with the use of quantum-mechanical Green's functions, it is convenient to regard the quantity $\mathbf{g}_{\sigma\sigma'} = \mathbf{g}_{\sigma\sigma'}' \frac{iaq}{\omega(\mathbf{q})} \sqrt{\frac{1}{M}}$, which weakly depends on $\mathbf{q}$, as an interaction constant. It is also convenient to combine the multiplier $\sqrt{\omega(\mathbf{q})/2}$ with the operator $\left(b_{\mathbf{q}} + b_{-\mathbf{q}}^+ \right)$ and determine Green's function on the basis of the operators $\gamma_{\mathbf{q}} = \sqrt{\omega(\mathbf{q})/2} \left(b_{\mathbf{q}} + b_{-\mathbf{q}}^+ \right)$ and Hermitian conjugate ones, $\gamma_{\mathbf{q}}^+$.

Hence, it turns out that, in our model, there may exist three forms of electron-phonon interaction: the intraband interaction with the interaction constant g_{11}, intraband with the constant g_{22}, and interband one with the constant $g_{12} = g_{21} = g_0$. On the basis of what was said in Introduction, one should expect that a structural phase transition is possible in the system, provided that the constant g_{12} is large enough. The interactions associated with the constants g_{11} and g_{22} result in the scattering of charge carriers in each of two bands by transverse acoustic phonons.

3. Equilibrium Thermodynamic Potential in the Model of Interband Interaction of Electrons with Transverse Acoustic Phonons

Consider a correction to the thermodynamic potential of the system of electrons and phonons that arises owing to their interband interaction. The latter is described by the operator

$$H_{\text{int}} = (4N)^{-1/2} \sum_{\mathbf{k},\mathbf{q}} g_0(\mathbf{q}) \sqrt{\omega_0(\mathbf{q})/2} [a_2^+(\mathbf{k}+\mathbf{q})a_1(\mathbf{k}) +$$

$$+ a_1^+(\mathbf{k}+\mathbf{q})a_2(\mathbf{k})] (b_{\mathbf{q}} + b_{-\mathbf{q}}), \qquad (11)$$

where, analogously to Eq. (3), $b_{\mathbf{q}}$ and $b_{\mathbf{q}}^+$ are the operators of annihilation and creation, respectively, of phonons with the momentum $\mathbf{q}$ and the frequency $\omega_0(\mathbf{q})$; $g_0(\mathbf{q})$ is the constant of their interband interaction with electrons in the valence (subscript 1) and conduction (subscript 2) bands; the corresponding fields are described by the operators of creation, $a_\sigma^+(\mathbf{k})$, and annihilation, $a_\sigma(\mathbf{k})$, of electrons with one-particle energies $E_\sigma(\mathbf{k})$ ($\sigma = 1, 2$). The expression for the Hamiltonian H_0 of the free fields of electrons and phonons looks like formula (3).

A very convenient relation between the sought correction and the temperature Green's functions of phonons was given in monograph [8]. It reads

$$\Delta\Omega = T \sum_{\mathbf{q}} \int_0^{g_0(\mathbf{q})} \frac{dg}{g} \sum_{\omega_n} \frac{\omega_n^2 + \omega_0^2(\mathbf{q})}{\omega_0^2(\mathbf{q})} [D(\mathbf{q}, \omega_n) -$$

$$- D^{(0)}(\mathbf{q}, \omega_n)], \qquad (12)$$

where $\omega_n = 2\pi nT$, and n is an integer. Green's function of phonons that takes the interaction into account, $D(\mathbf{q}, \omega_n)$, is related to Green's function of noninteracting phonons,

$$D^{(0)}(\mathbf{q}, \omega_n) = \omega_0^2(\mathbf{q}) \left[(i\omega_n)^2 - \omega_0^2(\mathbf{q}) \right]^{-1},$$

by the Dyson equation,

$$D(\mathbf{q}, \omega_n) = D^{(0)}(\mathbf{q}, \omega_n) +$$

$$+ D^{(0)}(\mathbf{q}, \omega_n) P(\mathbf{q}, \omega_n) D(\mathbf{q}, \omega_n), \qquad (13)$$

where $P(\mathbf{q}, \omega_n)$ is the polarization operator of phonons. Therefore, it is more convenient to present

Eq. (12) in the form

$$\Delta\Omega = T \sum_{\mathbf{q}} \int_0^{\mathrm{g}_0(\mathbf{q})} \frac{d\mathrm{g}}{\mathrm{g}} \sum_n \omega_0^2(\mathbf{q}) P(\mathbf{q}, \omega_n) \{(i\omega_n)^2 -$$

$$- \omega_0^2(\mathbf{q}) [1 + P(\mathbf{q}, \omega_n)]\}^{-1}. \tag{14}$$

The first, most essential terms of the second order in the perturbation theory series for the polarization operator of phonons $P(\mathbf{q}, \omega_n)$ with respect to the interaction can be presented by two Feynman's diagrams. The latter differ from each other by the permutation of indices 1 and 2 that enumerate the valence and conduction bands, respectively. According to the correspondence rules [11], the polarization operator that corresponds to those two diagrams in the second order of perturbation theory, has the following analytical form:

$$P'(\mathbf{q}, \omega_n) = 2TN^{-1}\mathrm{g}^2 \sum_{\mathbf{k}\omega_m} \psi(i\omega_n, i\omega_m, \mathbf{k}, \mathbf{q}), \tag{15}$$

$$\psi(i\omega_n, i\omega_m, \mathbf{k}, \mathbf{q}) =$$

$$= [i\omega_m - E_2(\mathbf{k})(i(\omega_n + \omega_m) - E_1(\mathbf{k} + \mathbf{q}))]^{-1} +$$

$$+ [i\omega_m - E_1(\mathbf{k})(i(\omega_n + \omega_m) - E_2(\mathbf{k} + \mathbf{q}))]^{-1}, \tag{16}$$

where $\omega_m = (2m + 1)\pi T$, and m is an integer.

One can easily see that the sum over ω_m in Eq. (15) is a sum of residues at the poles of the auxiliary function $f(\omega) = -T^{-1}\{\exp(\omega/T) + 1\}^{-1}$ that enters the integrand of the integral

$$\oint_{C_R \to \infty} d\omega f(\omega) \psi(i\omega_n, \omega, \mathbf{k}, \mathbf{q}) \tag{17}$$

along the circle of infinite radius in the plane of the complex variable ω. The integrand in Eq. (17) tends to zero at $\omega \to \infty$ not slower than ω^{-2}. Therefore, integral (17) equals zero, and, hence, the indicated sum of residues is equal to the negative sum of residues at the poles of the function $\psi(i\omega_n, \omega, \mathbf{k}, \mathbf{q})$ in the complex plane ω. Hence, the infinite sum over ω_m in Eq. (15) can be substituted by the expression

$$-f(E_2(\mathbf{k}))[i\omega_n + E_2(\mathbf{k}) - E_1(\mathbf{k} + \mathbf{q})]^{-1} +$$

$$+ f(E_1(\mathbf{k} + \mathbf{q}) - i\omega_n)[i\omega_n + E_2(\mathbf{k}) - E_1(\mathbf{k} + \mathbf{q})]^{-1} -$$

$$- f(E_1(\mathbf{k}))[i\omega_n + E_1(\mathbf{k}) - E_2(\mathbf{k} + \mathbf{q})]^{-1} +$$

$$+ f(E_2(\mathbf{k} + \mathbf{q}) - i\omega_n)[i\omega_n + E_1(\mathbf{k}) - E_2(\mathbf{k} + \mathbf{q})]^{-1}. \tag{18}$$

Expressions (18) and (15) become much simpler for a crystal with a wide energy gap:

$$T^{-1}\{[E_1(\mathbf{k} + \mathbf{q}) - i\omega_n - E_2(\mathbf{k})]^{-1} +$$

$$+ [i\omega_n + E_1(\mathbf{k}) - E_2(\mathbf{k} + \mathbf{q})]^{-1}\}, \tag{19}$$

$$P'(\mathbf{q}, i\omega_n) = 4\mathrm{g}^2\bar{\Delta}(\mathbf{q})\left[(i\omega_n)^2 - \bar{\Delta}^2(\mathbf{q})\right]^{-1}, \tag{20}$$

where the quantity $\bar{\Delta}(\mathbf{q})$ obtained by summing up the differences $E_2(\mathbf{k}) - E_1(\mathbf{k} + \mathbf{q})$ over $\mathbf{k}$ and dividing the result by N can be called the average interband distance between those sublevels in two electron energy bands, the momenta of which differ by the vector $\mathbf{q}$.

Substituting Eq. (20) into Eq. (14), we obtain

$$\Delta\Omega = -T \sum_{\mathbf{q}} \int_0^{\mathrm{g}(\mathbf{q})} d\mathrm{g} 4\mathrm{g}\omega_0^2(\mathbf{q})\bar{\Delta}(\mathbf{q}) \times$$

$$\times \sum_n \left\{ \left[(i\omega_n)^2 - \bar{\Delta}^2(\mathbf{q})\right]\left[(i\omega_n)^2 - \omega_0^2(\mathbf{q})\right] -$$

$$- 4\mathrm{g}^2\omega_0^2(\mathbf{q})\bar{\Delta}(\mathbf{q}) \right\}^{-1}. \tag{21}$$

The summation over n in Eq. (21) is carried out similarly to that in Eq. (15) with the help of the auxiliary function $\varphi(\omega) = T^{-1}\{\exp(\omega/T) - 1\}^{-1}$. The result is determined by the position of poles of the function

$$\psi'(\omega, \mathbf{q}) = \left\{ \left[\omega^2 - \bar{\Delta}^2(\mathbf{q})\right]\left[\omega^2 - \omega_0^2(\mathbf{q})\right] -$$

$$- 4\mathrm{g}^2\omega_0^2(\mathbf{q})\bar{\Delta}(\mathbf{q}) \right\}^{-1}.$$

If the energy gap is so wide that $\bar{\Delta}(\mathbf{q}) \gg \omega_0(\mathbf{q})$, the positions of its four poles are determined by the equalities

$$\begin{cases} \omega^2 = \omega_1^2(\mathbf{q}) \approx \bar{\Delta}^2(\mathbf{q}) + 4\mathrm{g}^2\omega_0^2(\mathbf{q})\bar{\Delta}^{-1}(\mathbf{q}) \approx \bar{\Delta}^2(\mathbf{q}), \\ \omega^2 = \omega_2^2(\mathbf{q}) \approx \omega_0^2(\mathbf{q})\left[1 - 4\mathrm{g}^2/\bar{\Delta}(\mathbf{q})\right], \end{cases} \tag{22}$$

Then, quantity (21) reads

$$\Delta\Omega = -\sum_{\mathbf{q}} \int_0^{\mathrm{g}_0(\mathbf{q})} 2\mathrm{g}d\mathrm{g}\left[2n(\omega_2(\mathbf{q}), T) + 1\right] \times$$

$$\times \omega_0^2(\mathbf{q})\bar{\Delta}^{-1}(\mathbf{q})\omega_2^{-1}(\mathbf{q}), \tag{23}$$

where

$$n(\omega_2(\mathbf{q}),\, T) = T\varphi(\omega_2(\mathbf{q})) = \exp(\omega_2(\mathbf{q})/T - 1)^{-1}.$$

The second equality in Eqs. (22) demonstrates that, in the applied approximation, the square of the phonon frequency, being renormalized by the interaction, can become negative, which testifies to the instability of the high-symmetry phase at $4g_0^2(\mathbf{q}) > \bar{\Delta}(\mathbf{q})$, i.e. if the interaction is strong enough. Since the quantity $\bar{\Delta}(\mathbf{q})$ has a magnitude of an order of 1 eV for the considered crystals, the quantity $g_0^2(\mathbf{q})$ can expectedly be equal to and even slightly exceed the quantity $\bar{\Delta}(\mathbf{q})/4$ in rare substances and for phonon modes in a small vicinity of a certain point in the first Brillouin zone. It is just this case where the phase transitions into an ordered phase under the action of the electron-phonon interaction become probable. In addition, it is this case where two terms in expression (22) for $\omega_2^2(\mathbf{q})$ turn out to have approximately the same magnitude. Therefore, it is necessary to consider a correction of the fourth order to the polarization operator. According to work [4], if this correction is made allowance for, we obtain

$$\omega_2^2(\mathbf{q}) = \omega_0^2(\mathbf{q}) \left[1 - 4g^2/\bar{\Delta}(\mathbf{q}) + 48g^4 T/2\bar{\Delta}^3(\mathbf{q})\right]. \tag{24}$$

In this new approximation, the frequency $\omega_2(\mathbf{q})$ vanishes at

$$T = T_c(\mathbf{q}) = \left[4g_0^2(\mathbf{q}) - \bar{\Delta}(\mathbf{q})\right]\bar{\Delta}^2(\mathbf{q})/24g_0^4(\mathbf{q}) \tag{25}$$

provided that $g_0(\mathbf{q})$ is used instead of g, whereas it is positive at $T > T_c(\mathbf{q})$. However, frequency (24) enters the integrand of Eq. (23). The involved integral over g in Eq. (13) can be considerably simplified. Let the quantity on the right-hand side of Eq. (25) be positive only for one mode with the wave vector $\mathbf{q}_0$. Consider the term in Eq. (23) that corresponds to $\mathbf{q}_0$. Let $T_c(\mathbf{q}_0)$ be substantially larger than the frequency $\omega_2(\mathbf{q}_0)$ calculated according to formula (24) with the coupling constant $g_0(\mathbf{q}_0)$. Then, at $T > T_c(\mathbf{q}_0)$, we obtain

$$\coth\frac{\omega_2(\mathbf{q}_0)}{T} = 2n(\omega_2(\mathbf{q}_0),T) + 1 \approx 2T/\omega_2(\mathbf{q}_0). \tag{26}$$

In this case, the integral over g in the corresponding term in Eq. (23) can be easily calculated. As a result,

at $t \equiv T - T_c \ll T_c \ll \frac{1}{6}\bar{\Delta}$, we obtain

$$\Delta\Omega(q_0) = -\frac{T_c}{2}\ln\frac{3t}{2\bar{\Delta}}. \tag{27}$$

This relation resolves the problem of the thermodynamic potential peculiarity at the point of PT2, put forward by L.D. Landau [4]. Together with the results obtained while considering this peculiarity by L. Onsager in the framework of the Ising model [12] and when analyzing this peculiarity in the case of ferroelectric transition [3], relation (27) allows us to assert that the logarithmic peculiarity at the point T_c in the thermodynamic potential is inherent to every PT2. Since the logarithm in Eq. (27) is negative, the quantity $\Delta\Omega(q_0)$ increases if $T \to T_c$. This growth becomes interrupted owing to the vanishing of the soft-mode frequency (24) and the appearance of coherent displacements of ions (i.e. the quantum average displacements of ions). At $q_0 = 0$, those displacements are uniform over the crystal volume.

If the interaction is weak, so that $\bar{\Delta} > 4g^2$ for all modes, the expression for $\Delta\Omega$ contains no diverging terms, and the others can be easily evaluated supposing that

$$\omega_2^2(\mathbf{q}) = \omega_0^2(\mathbf{q})\left[1 - 4g^2(\mathbf{q})\bar{\Delta}^{-1}(\mathbf{q})\right]. \tag{28}$$

However, the number of those terms in sum (13) is tremendous even for a millimeter-sized crystal (of an order of 10^{20} in the latter case). Therefore, a single singular term of types (19) or (20) can be observed against a huge number of non-singular terms only provided that the ratio $t/\bar{\Delta}$ is negligibly small. Of course, changing from the sum in Eq. (23) – which must be a sum owing to the finiteness of motion of considered quasiparticles – to the integral, we obtain a non-diverging thermodynamic potential, which can be used at temperatures that practically approach T_c as close as possible, and, hence, the regular expansions of the thermodynamic potential at those temperatures in an order-parameter series according to Landau's theory of phase transitions of the second kind become possible.

4. Thermodynamic Potential of the System in the Ordered Phase

The method used above cannot be applied to the calculation of $\Delta\Omega$ at $t < 0$, because the coherent displacements of equilibrium atomic positions in the

crystal that take place at the PT2 change the crystal symmetry, with the thermal and quantum-mechanical fluctuations making the problem even more complicated. However, we can determine the value of thermodynamic potential at $T = 0$ K (when thermal vibrations of atoms are absent, and the entropy of the system equals zero) as the average value of Hamiltonian (3) for a crystal state with a deformed lattice. Taking into account that the electron processes in our system with a wide energy gap develop within a time interval of an order of 10^{-15} s, and the phonon ones run within a time interval of an order of 10^{-13} s, the system state vector can be presented in the adiabatic approximation as a product, $|U|0\rangle\psi \equiv |d,\psi\rangle$. Here, ψ is the state vector for the electron subsystem (for the sake of simplicity, we neglect the spin variable), and $U = \prod_{\mathbf{q}} \exp(d_{\mathbf{q}} b_{\mathbf{q}}^+ - d_{\mathbf{q}}^* b_{\mathbf{q}})$, where $d_{\mathbf{q}}$ are complex numbers, is the unitary operator of deformation that acts on the ground-state vector $|0\rangle$ of the phonon field.

From the theory of quantum-coherent states of Bose fields [13, 14], it is known that $U b_{\mathbf{q}} U^+ = b'_{\mathbf{q}} = b_{\mathbf{q}} + d_{\mathbf{q}}$ and $b_{\mathbf{q}}^{'+} = b_{\mathbf{q}}^+ + d_{\mathbf{q}}^*$. Therefore, the average value $\langle 0|U|b_{\mathbf{q}}|U^+|0\rangle$ is equal to the number $d_{\mathbf{q}}$, because $\langle 0|b_{\mathbf{q}}|0\rangle = 0$. Of course, $\langle 0|U|b_{\mathbf{q}}^+|U^+|0\rangle = d_q^*$, and the average deviation of the equilibrium atomic position along the normal coordinate of the $\mathbf{q}$-th vibration mode from that in the symmetric configuration with the inversion center is equal to $\bar{\lambda}_{\mathbf{q}} = \sqrt{\frac{1}{2}M_{\mathbf{q}}\omega(\mathbf{q})}(d_{\mathbf{q}}^* + d_{\mathbf{q}})$, where $M_{\mathbf{q}}$ is the reduced mass of the indicated vibration mode. Hence, the real parts of $d_{\mathbf{q}}$ characterize a deformation of the crystal lattice. The transformation of the Hamiltonian H with the use of the unitary operator U shows that the state of any quantum-mechanical harmonic oscillator can change owing to either a variation in the number of oscillation quanta or a displacement of the equilibrium position characterized by the parameter $d_{\mathbf{q}}$ [13, 14]. The avarage value of total Hamiltonian (3) in the state $|d,\psi\rangle$ can be expressed in the form

$$
\bar{H} = \sum_{k,\sigma=1}^{2} E_{\sigma}(\mathbf{k})\langle\psi|a_{\sigma k}^+ a_{\sigma k}|\psi\rangle + \sum_{\mathbf{q}}\Big\{\omega(\mathbf{q})d_{\mathbf{q}}^+ d_{\mathbf{q}}
$$

$$
+ \sum_{k,\sigma\neq\sigma'} \sqrt{\frac{\omega(\mathbf{q})}{2N}} g_0(\mathbf{q})\langle\psi|a_{k\sigma}^+ a_{k-q\sigma'}|\psi\rangle(d_{\mathbf{q}} + d_{-\mathbf{q}}^+)\Big\},
\tag{29}
$$

because the average number of real quanta in the state $|d,\psi\rangle$ equals zero. Since the numbers $d_{\mathbf{q}}$ can be selected infinitesimally small, the harmonic oscillator energy can be changed by any small value by shifting the equilibrium positions. The actual energy of the system in the ground state corresponds to the minimum value of $\bar{H}$ obtained at varying the state $|d,\psi\rangle$.

For the variation procedure to be convenient, let us express the complex numbers $d_{\mathbf{q}}$ in terms of their absolute values $|d_{\mathbf{q}}|$ and phases $\varphi_{\mathbf{q}}$. Equating the derivative of function (29) with respect to $|d_{\mathbf{q}}|$ to zero, we determine the extremum,

$$
\bar{H} = \sum_{k,\sigma=1}^{2} E_{\sigma}(\mathbf{k})\langle\psi|a_{\sigma k}^+ a_{\sigma k}|\psi\rangle - \sum_{\mathbf{q}}\{\omega(\mathbf{q})|d_{\mathbf{q}}|^2,
$$

$$
|d_{\mathbf{q}}| = -\frac{\cos\varphi(\mathbf{q})}{\sqrt{2N\omega(\mathbf{q})}} \sum_{k,\sigma\neq\sigma'} g_0(\mathbf{q})\langle\psi|a_{\sigma k}^+ a_{\sigma k}|\psi\rangle,
\tag{30}
$$

which corresponds to a minimum if $\cos\varphi(\mathbf{q}) = -1$. Relations (30) clearly show that the interaction energy between electrons and a coherent deformation is negative, being twice as large by the absolute value in comparison with the deformation energy.

A common practice in the theory of phase transitions under the influence of the electron-phonon interaction consists in that the simplest case is considered, where the strong interaction includes only the interaction between electrons and phonons with the momentum $\mathbf{q} = 0$. For this case, according to Eq. (30),

$$
d_0 = (2N\omega_0(0))^{-1/2} g_0 \sum_k \langle\psi|a_{\sigma k}^+ + a_{\sigma k}|\psi\rangle.
\tag{31}
$$

The wave functions of the electron subsystem in the case where the interband electron-phonon interaction accompanied by the transfer of the zero momentum to phonons takes place should be superpositions of two Bloch wave functions from different electron bands with the same momentum depending on the variable superposition coefficients C_{nm} ($m, n = 1, 2$). Then, introducing the notation $\Delta(\mathbf{k}) = E_2(\mathbf{k}) - E_1(\mathbf{k})$ and taking into account that $\sum_{m=1}^{2}|C_{nm}|^2 = 1$, we obtain, instead of relation (30),

$$
|d_{\mathbf{q}}| = 2N^{1/2} g_0(2\omega(0))^{-1/2}|C_{12}|\sqrt{1-|C_{12}|^2},
\tag{32}
$$

$$
\bar{H} = \sum_k E_1(\mathbf{k}) + |C_{12}|^2 N(\bar{\Delta} - 2g_0^2) + 2Ng_0^2|C_{12}|^4,
\tag{33}
$$

where $\bar{\Delta} = N^{-1} \sum_k \Delta(\mathbf{k})$. Varying $\bar{H}$ with respect to the parameter $|C_{12}|^2$, we find that the minimum of $\bar{H}$ is attained at $|C_{12}|^2 = \frac{2g_0^2 - \bar{\Delta}}{4g_0^2}$ and $|C_{11}|^2 = \frac{2g_0^2 + \bar{\Delta}}{4g_0^2}$. The energy minimum, i.e. the energy of the system in the ground state E_0, is equal to

$$E_0 = \sum_k \left\{ E_1(\mathbf{k}) - \frac{(2g_0^2 - \bar{\Delta})^2}{8g_0^2} \right\} = \sum_k E_1(\mathbf{k}) + \Delta E_0$$

(34)

at $T = 0$ K, where ΔE_0 is the interaction-induced addition to the ground-state energy. According to Eq. (32), the energy minimum is related to the value

$$d_0 = N^{1/2} \sqrt{\frac{4g_0^4 - \bar{\Delta}^2}{8\omega(0)g_0^2}}. \tag{35}$$

For the ground state of the system with energy (34) to be realized, the condition of strong coupling,

$$2g_0^2 > \bar{\Delta}, \tag{36}$$

must be obeyed, under which the quantity $|C_{12}|^2$ is positive, indeed.

If we assume, by analogy with work [8], that the electron spin can have two possible orientations in every state of the valence and conduction bands, condition (36) should be simply substituted by the condition $4g_0^2 > \bar{\Delta}$. In such a manner, the method of varying the states in the electron and phonon subsystems used by us in the case of a strong interband electron-phonon coupling allowed a relation between the lattice deformation parameter (this is value (35) of the parameter d_0) at $T \to 0$ K and the modification of the electron distribution function in a unit cell owing to the entanglement between the electron states in the conduction and valence bands to be established.

Moreover, the calculated ground-state energy (Eq. (34)) shows that, due to the interaction between a deformation and electrons, every sublevel in the valence band drops by the value $\Delta E = -\frac{(2g_0^2 - \bar{\Delta})^2}{8g_0^2}$. The corresponding magnitude turns out of an order of 10^{-4} eV at $T_c/\bar{\Delta} \approx 0.01$ and $T_c = 400$ K, being an extreme (at $T = 0$ K) addition to the thermodynamic potential of the free electron and phonon interaction fields.

At $T = 0$ K, the entropy equals zero, and the thermodynamic potential in $\bar{H}$ equals E_0. Therefore, beyond the Ginzburg region at $T < T_c$, expression (35)

for the average energy can be regarded as the dependence of the thermodynamic potential of the whole system on the order parameter $|C_{12}|$ in the Landau theory for PT2. This is the more so because, according to Eq. (34), in our model of the displacement-type phase transition, the parameter $|C_{12}|^2$ characterizes the magnitude of equilibrium position displacements along the corresponding normal coordinate. Therefore, according to the Landau theory, the expansion of the thermodynamic potential in our model beyond the Ginzburg region in the interval $T < T_d$ has the form

$$\Omega = \sum_k E_1(\mathbf{k}) + \alpha(T - T_c)|C_{12}|^2 + 2Ng_0^2|C_{12}|^4.$$

Hence, at $T = 0$ K, we obtain $\alpha = -\frac{N}{T_c}(\bar{\Delta} - 2g_0^2)$. In the situation with "non-fixed" spins, this formula for the determination of the parameter α is substituted by the following one:

$$\alpha = -\frac{N}{T_c}(\bar{\Delta} - 4g_0^2). \tag{37}$$

Relation (37) allows one, when knowing the experimentally found coefficient α of the Landau theory and the parameter $\bar{\Delta}$, to determine the electron-phonon interaction constant $\bar{g}_0$ and compare it with the corresponding estimates.

5. Conclusion

Hence, PT2 associated with the interband electron-phonon interaction stems from a logarithmic singularity of the thermodynamic potential in a small vicinity of the transition point T_c. As a result, the new phase with nonzero displacements of the equilibrium positions of ions turns out thermodynamically more beneficial. It can be demonstrated [3, 8] that just the interaction of electrons with those displacements makes the crystal energy lower.

It is of importance that the possible lattice vibration modes compose an almost continuous spectrum in any crystal, even in a micro-sized one. Therefore, the assumption that the right-hand side of equality (25) is positive only for one mode with the wave vector $\mathbf{q}_0$ is doubtful. If the mode spectrum is continuous, and if this condition is satisfied for a certain $\mathbf{q} = \mathbf{q}_0$, it must also be satisfied for the wave vectors $\mathbf{q}$ in some vicinity of $\mathbf{q}_0$. Let the quantity $\chi(\mathbf{q}) \equiv 4g^2(\mathbf{q}) - \bar{\Delta}(\mathbf{q})$ possess a maximum at $\mathbf{q} = \mathbf{q}_0$.

Its expansion in the variable $|\mathbf{q} - \mathbf{q}_0|$ in a vicinity of the point $\mathbf{q} = \mathbf{q}_0$ looks like $\chi(\mathbf{q}) \equiv \alpha - \beta|\mathbf{q} - \mathbf{q}_0|^2$, where $\alpha = 4\mathrm{g}^2(\mathbf{q}_0) - \bar{\Delta}(\mathbf{q}_0)$, and β can depend on the direction of the vector $\mathbf{q}$. If β weakly depends on the $\mathbf{q}$-direction, the density of active mode numbers in the interval of positive χ-values tends to infinity at $\chi \to \alpha$. Therefore, the frequencies of a large number of active vibration modes vanish in a nearest vicinity of $T_c(\mathbf{q}_0)$, whereas the frequencies of other active modes will vanish at lower temperatures, which follows from Eq. (25). As was shown in work [8], the frequency of every soft mode, after having passed through the zero value at the corresponding temperature T_c, grows owing to the interaction with emerging coherent displacements of atoms in the crystal lattice in the temperature interval $T < T_c$. Therefore, the temperature behavior of the frequencies of active modes results in a change of their dispersion, when the temperature varies in a vicinity of $T_c(\mathbf{q}_0)$. Since the constant of the electron coupling with transverse acoustic phonons is maximal at $q \approx \pi/a$, i.e. near the first Brillouin zone boundary, the magnitude of q_0 is also of the order of π/a.

According to the theory expounded above, the variation in the dispersion of acoustic vibration frequencies at the temperature change can be observed experimentally if the macrostates are quasiequilibrium at every temperature, which is quite illusive. It is so because the thermodynamic potential logarithmically diverges if some frequencies of active modes become zero. At the same time, the zeroing of a certain acoustic mode frequency means that the relaxation time for the displacements of equilibrium atomic positions in the crystal lattice along the normal coordinate of this mode becomes infinite. Therefore, the corresponding state of crystal lattice is not quasiequilibrium. All that gives rise to a situation where a metastable coherent displacement along the normal coordinate of $\mathbf{q}_0$-mode, which emerged at $T > T_c(\mathbf{q}_0)$ owing to fluctuations, can survive, by very slowly relaxing, as the temperature decreases below $T < T_c(\mathbf{q}_0)$, and can become a stable structure (a domain). The frequency of vibrations along the indicated normal coordinate in this structure does not vanish at the temperature $T_c(\mathbf{q}_0)$. Therefore, the zeroing of some mode frequencies may probably turn out unobservable at all.

The changes in the dispersion of acoustic phonons at the phase transition of the second kind, which was predicted by us, can be detected experimentally using the method of electron scattering by phonons.

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ПРО РОЛЬ ФЛУКТУАЦІЙ КОГЕРЕНТНИХ
ЗСУВІВ ПОЛОЖЕННЯ РІВНОВАГИ АТОМІВ
ПРИ ФАЗОВИХ ПЕРЕХОДАХ ДРУГОГО РОДУ

Р е з ю м е

Теоретично досліджено фазові переходи другого роду в фероіках типу сегнетоеластики. Розглянуто перехід при зниженні температури в кристалах з широкою забороненою зоною, зумовлений взаємодією електронів з однією гілкою поперечних акустичних коливань кристалічної ґратки. Розраховано вершинну частину цієї взаємодії з поперечними коливаннями. Обговорено особливості термодинамічного потенціалу в точці переходу і температурну залежність дисперсії акустичних фононів при переході за квазірівноважними станами. Показано, що стабілізація електронної підсистеми структурних флуктуацій у високосиметричній фазі і зменшення частот м'яких мод роблять такі флуктуації метастабільними.