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ON THE APPLICATION OF THE UNIFIED MODEL OF FERROELECTRIC PHASE TRANSITION TO CRYSTALS WITH COMPLEX STRUCTURE

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The model of ferroelectric phase transition in a crystal with complex structure is considered. The basic equations decribing the phase transition in the framework of a self-consistent scheme are derived. A simple model with two atoms in a unit cell is discussed in some detail. It is shown that the low-temperature phase is ferro- or antiferroelectrically ordered, depending on the model parameters. In both cases, the phase transition occurs without change in translational symmetry. The behaviour of electrical susceptibility in the case of the second-order phase transition is discussed and it is shown that the results are similar to those of the phenomenological theory.

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1. *Introduction*

In ferroelectric crystals there is an usually distinguished group of atoms which are active in the phase transition. The phase transition can be a result of spontaneous displacements of active atoms or their ordering between equivalent equilibrium positions. Therefore, the phase transitions are considered as being of the displacement type or order-disorder type, respectively [1]. Such a description is, however, a simplified one and does not reflect the whole complexity of phase transitions in real crystals (see e.g. [2]). Recently, Stamenkovic et al. [3] have proposed the so-called unified model (UM) of ferroelectric phase transitions. In the framework od this model the behaviour characteristics of the order-disorder type as well as of the displacement type for phase transitions was taken into account. It was shown that the phase transition may be of the order-disorder, displacement or mixed types, depending on the model parameters.

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The ferroelectric crystals have, as a rule, a very complicated crystal structure. Therefore, different crystal units may be active in the ferroelectric phase transition. Such a situation appears probably in the TGS crystal where the glycine group and SO_4 complex motions are important for the phase transition [4, 5]. In the well known ferroelectric, KDP, the protons in the hydrogen bonds and PO_4 complexes are active in the phase transition [6]. On the other hand, in antiferroelectric crystals one distinguishes in the ordered phase, at least two non-equivalent groups of atoms which are active in the phase transition.

The aim of this paper is to discuss such a model which would be helpful in describing the phase transitions in the above mentioned crystals. In our considerations we take as a starting point the model presented in Ref. [3]. Therefore, we extend UM to the case of many active atoms within the unit cell. The model with two non-equivalent atoms is discussed in some aspects. We use the methods of calculation described in [3]. We also discuss the behaviour of the electric susceptibility for the second order phase transitions and compare the results with those of the phenomenological theory.

The paper is organized as follows: in Section 2 a Hamiltonian of the model is presented. Equilibrium conditions of the system are derived in Section 3. In Sections 4 and 5 the properties of the phonon and pseudospin subsystems are investigated. The Green's functions are determined in the self-consistent phonon approximation. The mean values of pseudospin operators are found with the use of the Bogolubov variational method in Section 5. In Section 6 a model of the two-sublattice ferroelectric is discussed. The behaviour of the electric susceptibility of such a model is considered in Section 7. Final remarks are presented in Section 8.

2. *Hamiltonian of the model*

Let us consider a complex crystal with N unit cells, volume $V = Nv$ and n atoms within the cell. We assume that atomic displacements occur along an arbitrary axis and that the single-particle potential has the shape of a symmetric double well. In the ordered phase the atom may be in the left- or in the right well. So the atomic coordinate is written as follows:

$$\boldsymbol{R}_{l\kappa} = \boldsymbol{R}^0_{l\kappa} + \sigma^+_{l\kappa}x^+_{l\kappa} + \sigma^-_{l\kappa}x^-_{l\kappa},$$

where l labels the lattice sites and $\kappa(= 1, 2, \ldots n)$ atoms within the unit cell. $\boldsymbol{R}^0_{l\kappa}$ denotes the equilibrium position in the high-temperature phase, $x^\alpha_{l\kappa}$ is taken from the local maximum point of the single-particle potential, $\sigma^\alpha_{l\kappa}$ is the projection operator with two eigenvalues $\sigma^\alpha_{l\kappa} = 1$ or 0, $(\alpha = \pm)$ corresponding to the cases where atom $l\kappa$ is placed in the α or $-\alpha$ well, respectively.

The Hamiltonian of the system takes the form [3, 7]

$$H = \sum_{l\kappa\alpha} \sigma^\alpha_{l\kappa}\left\{\frac{(p^\alpha_{l\kappa})^2}{2M_\kappa} - \frac{A_\kappa}{2}(x^\alpha_{l\kappa})^2 + \frac{B_\kappa}{4}(x^\alpha_{l\kappa})^4\right\}$$

$$+\frac{1}{4}\sum_{l\kappa\alpha}\sum_{l_1\kappa_1\beta} \Phi^{\kappa\kappa_1}_{ll_1}\sigma^\alpha_{l\kappa}\sigma^\beta_{l_1\kappa_1}(x^\alpha_{l\kappa} - x^\beta_{l_1\kappa_1})^2, \tag{2.1}$$

where $p^{\alpha}_{l\kappa}$ is the momentum of the atom $l\kappa$ in the α state, M_{κ} and $\Phi^{\kappa\kappa_1}_{ll_1}$ are respectively the masses and force constants in the system, $x^{\alpha}_{l\kappa}$ is the sum of static displacement, x^{α}_{κ}, and thermal fluctuation $u^{\alpha}_{l\kappa}$

$$x^{\alpha}_{l\kappa} = \langle x^{\alpha}_{l\kappa}\rangle + u^{\alpha}_{l\kappa} \equiv x^{\alpha}_{\kappa} + u^{\alpha}_{l\kappa},$$

where $\langle\ldots\rangle = \mathrm{Tr}\,\{\ldots\exp(-H/\Theta)\}/\mathrm{Tr}\,\{\exp(-H/\Theta)\}$ denotes thermal average with the Hamiltonian (2.1).

Expressing the projection operator by means of the spin operator, according to

$$\sigma^{\alpha}_{l\kappa} = \tfrac{1}{2}(1+\alpha\sigma_{l\kappa}),$$

we write the Hamiltonian (2.1) in the form

$$H = H_L + H_{L\sigma} = \tfrac{1}{2}\sum_{l\kappa\alpha}\left\{\frac{(p^{\alpha}_{l\kappa})^2}{2M_{\kappa}} - \frac{A_{\kappa}}{2}(x^{\alpha}_{l\kappa})^2 + \frac{B_{\kappa}}{4}(x^{\alpha}_{l\kappa})^4\right\}$$

$$+\tfrac{1}{16}\sum_{\substack{l\kappa\alpha\\ l_1\kappa_1\beta}}\Phi^{\kappa\kappa_1}_{ll_1}(x^{\alpha}_{l\kappa}-x^{\beta}_{l_1\kappa_1})^2 + \sum_{l\kappa} h_{l\kappa}\sigma_{l\kappa} - \tfrac{1}{2}\sum_{\substack{l\kappa\\ l_1\kappa_1}} J^{\kappa\kappa_1}_{ll_1}\sigma_{l\kappa}\sigma_{l_1\kappa_1}, \tag{2.2}$$

where

$$J^{\kappa\kappa_1}_{ll_1} = -\tfrac{1}{8}\sum_{\alpha\beta}\Phi^{\kappa\kappa_1}_{ll_1}\alpha\beta(x^{\alpha}_{l\kappa}-x^{\beta}_{l_1\kappa_1})^2$$

plays the role of an "exchange integral", and

$$h_{l\kappa} = \tfrac{1}{2}\sum_{\alpha=\pm}\left\{\frac{(p^{\alpha}_{l\kappa})^2}{2M_{\kappa}} - \frac{A_{\kappa}}{2}(x^{\alpha}_{l\kappa})^2 + \frac{B_{\kappa}}{4}(x^{\alpha}_{l\kappa})^4\right\}\alpha + \tfrac{1}{8}\sum_{l_1\kappa_1\alpha\beta}\Phi^{\kappa\kappa_1}_{ll_1}\alpha(x^{\alpha'}_{l\kappa}-x^{\beta}_{l_1\kappa_1})^2$$

may be considered as a mean field [3] (in analogy with the Ising model with many spins in a unit cell).

3. *The equilibrium conditions*

The static displacements x^{α}_{κ} can be calculated from the equilibrium condition [3]

$$i\frac{\partial}{\partial t}\langle p^{\alpha}_{l\kappa}(t)\rangle = \langle[p^{\alpha}_{l\kappa}, H]\rangle = 0, \tag{3.1}$$

where $p^{\alpha}_{l\kappa}(t)$ is an operator in the Heisenberg representation ($\hbar = 1$).

In the pseudoharmonic approximation and weak interaction between the phonon and pseudospin subsystems, Eq. (3.1) takes the form (for details, see [3]):

$$B_{\kappa}(x^{\alpha}_{\kappa})^3 + \{3B_{\kappa}\langle(u^{\alpha}_{l\kappa})^2\rangle - A_{\kappa} + \sigma^{-}_{\kappa}\Phi^{\kappa\kappa}(0) + \sum_{\kappa_1}\Phi^{\kappa\kappa_1}(0)\}x^{\alpha}_{\kappa}$$

$$= \Phi^{\kappa\kappa}(0)\sigma^{-\alpha}_{\kappa}x^{-\alpha}_{\kappa} + \sum_{\kappa_1(\neq\kappa)}\Phi^{\kappa\kappa_1}(0)\,(\sigma^{+}_{\kappa_1}x^{+}_{\kappa_1} + \sigma^{-}_{\kappa_1}x^{-}_{\kappa_1}), \tag{3.2}$$

where

$$\sigma^{\alpha}_{\kappa} = \langle\sigma^{\alpha}_{l\kappa}\rangle, \qquad \Phi^{\kappa\kappa_1}(q) = \sum_{l_1}\Phi^{\kappa\kappa_1}_{ll_1}e^{iq(l-l_1)}.$$

The system of Eqs. (3.2) has a solution $x_\kappa^\alpha = 0$ corresponding to the high-temperature phase, and solutions $x_\kappa^\alpha \neq 0$. In the latter case the spontaneous polarization may be non-zero if at least one of the variables $\sigma_\kappa \neq 0$.

4. *Phonon subsystem*

Now we determine the dynamic properties of a system: the excitation spectrum and atomic displacement correlation functions. We apply the Green's function method [8]. Let us consider the following Green's function (GF), (see [3]):

$$G^\alpha_{l\kappa l_1\kappa_1}(t-t_1) := \langle\langle u^\alpha_{l\kappa}(t); u_{l_1\kappa_1}(t_1)\rangle\rangle$$
$$= \frac{1}{N}\sum_q e^{iq(l-l_1)}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\, G^\alpha_{q\kappa\kappa_1}(\omega)e^{-i\omega(t-t_1)}, \tag{4.1}$$

$\alpha(=\pm)$ denotes that atom $l\kappa$ is in an α well ($\sigma^\alpha_{l\kappa} = 1$). In the same approximation as used in Eq. (3.2), we obtain the following equation for GF:

$$M_\kappa\omega^2 G^\alpha_{q\kappa\kappa_1}(\omega) = \delta_{\kappa\kappa_1} - \sigma_\kappa^{-\alpha}\Phi^{\kappa\kappa}(q)G^{-\alpha}_{q\kappa\kappa_1}(\omega) + \{3B_\kappa[(x_\kappa^\alpha)^2 + \langle(u^\alpha_{l\kappa})^2\rangle]$$
$$-A_\kappa + \Phi^{\kappa\kappa}(0) - \Phi^{\kappa\kappa}(q)\sigma_\kappa^{-\alpha} + \sum_{\kappa'(\neq\kappa)}\Phi^{\kappa\kappa'}(0)\}G^\alpha_{q\kappa\kappa_1}(\omega)$$
$$-\sum_{\kappa'(\neq\kappa)}\Phi^{\kappa\kappa'}(q)\,\{\sigma^+_{\kappa'}G^+_{q\kappa'\kappa_1}(\omega) + \sigma^-_{\kappa'}G^-_{q\kappa'\kappa_1}(\omega)\}, \tag{4.2}$$

which can be written in the matrix form:

$$\hat{A}(q, \omega)G(q, \omega) = \delta,$$

where $\hat{A}[2n^2\times 2n^2]$ is a quasidiagonal matrix

$$A = \begin{bmatrix} A_1 & & 0 \\ & A_2 & \\ & & \ddots & \\ 0 & & & A_n \end{bmatrix}, \quad G = \begin{bmatrix} G^+_{11} \\ G^-_{11} \\ \vdots \\ G^-_{n1} \\ G^+_{12} \\ \vdots \\ G^+_{nn} \\ G^-_{nn} \end{bmatrix}, \quad \delta = \begin{bmatrix} 1 \\ 1 \\ 0 \\ \vdots \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 0 \\ \vdots \\ 1 \end{bmatrix}.$$

The phonon excitation spectrum is obtained from the following equation:

$$\det |\Lambda_\kappa(\boldsymbol{q}, \omega)| = 0,$$

because

$$\det |\Lambda_1(\boldsymbol{q}, \omega)| = \det |\Lambda_2(\boldsymbol{q}, \omega)| = \ldots = \det |\Lambda_n(\boldsymbol{q}, \omega)|.$$

Mixing excitations of noninteracting sublattices results from their interaction $\Phi_{ll_1}^{\kappa\kappa_1} \neq 0$.

The self-consistent equations for the high-temperature region (the classical case) take the form:

$$\langle (u_{l\kappa}^\alpha)^2 \rangle = \frac{1}{N} \sum_{\boldsymbol{q}} \int_0^\infty d\omega \,\mathrm{cth}\left(\frac{\omega}{2\Theta}\right) \left\{ -\frac{1}{\pi} \mathrm{Im}\, G_{\boldsymbol{q}\kappa\kappa}^\alpha(\omega + i\varepsilon) \right\}$$

$$\simeq -\frac{\Theta}{N} \sum_{\boldsymbol{q}} \mathrm{Re}\, G_{\boldsymbol{q}\kappa\kappa}^\alpha(0 + i\varepsilon). \tag{4.4}$$

$\langle (u_{l\kappa}^\alpha)^2 \rangle$ ought to be inserted into Eq. (3.2), then x_κ^α could be calculated. An independent determination of σ_κ enables one to reach the full self-consistency.

5. *Pseudospin subsystem*

The mean values of the pseudospin operators will be determined by using the Bogolubov variational method [3, 9, 10, 11]. The trial Hamiltonian H_0 is chosen in the form

$$H_0 = \tilde{H}_L + \tilde{H}_\sigma,$$

where $\tilde{H}_L$ is the effective pseudoharmonic Hamiltonian, and

$$\tilde{H}_\sigma = -\sum_{l\kappa} \tilde{K}_{l\kappa} \sigma_{l\kappa}.$$

From the stationary conditions for the free energy

$$\frac{\partial F_{\mathrm{trial}}}{\partial \tilde{K}_{l\kappa}} = 0,$$

we calculate the variational parameters $\tilde{K}_{l\kappa}$ and σ_κ

$$\tilde{K}_{l\kappa} = \sum_{l_1\kappa_1} \langle J_{ll_1}^{\kappa\kappa_1} \rangle_0 \sigma_{\kappa_1} - \langle h_{l\kappa} \rangle_0 \equiv \sum_{\kappa_1} J^{\kappa\kappa_1} \sigma_{\kappa_1} - h_\kappa, \tag{5.1}$$

$$\sigma_\kappa = \langle \sigma_{l\kappa} \rangle_0 = \mathrm{th}\left(\frac{\tilde{K}_{l\kappa}}{\Theta}\right), \tag{5.2}$$

where

$$J^{\kappa\kappa_1} = \tfrac{1}{4}\, \Phi^{\kappa\kappa_1}(0)\, (x_\kappa^+ - x_\kappa^-)\, (x_{\kappa_1}^+ - x_{\kappa_1}^-),$$

$$h_\kappa = -\tfrac{1}{4} A_\kappa \{ (x_\kappa^+)^2 - (x_\kappa^-)^2 + \langle (u_{l\kappa}^+)^2 \rangle - \langle (u_{l\kappa}^-)^2 \rangle \} + \tfrac{1}{8} B_\kappa \{ (x_\kappa^+)^4 - (x_\kappa^-)^4$$

$$+3[x_\kappa^+\langle(u_{l\kappa}^+)^2\rangle-x_\kappa^-\langle(u_{l\kappa}^-)^2\rangle+\langle(u_{l\kappa}^+)^2\rangle^2-\langle(u_{l\kappa}^-)^2\rangle^2]\}+\tfrac{1}{8}\sum_{l_1\kappa_1}\Phi_{ll_1}^{\kappa\kappa_1}\{2[(x_\kappa^+)^2$$
$$-(x_\kappa^-)^2+\langle(u_{l\kappa}^+)^2\rangle-\langle(u_{l\kappa}^-)^2\rangle+(x_\kappa^--x_\kappa^+)(x_{\kappa_1}^+-x_{\kappa_1}^-)]+\langle(u_{l\kappa}^--u_{l\kappa}^+)(u_{l_1\kappa_1}^+-u_{l_1\kappa_1}^-)\rangle\}.$$

For the phase transitions of the order-disorder type the atomic vibrations are usually neglected, $u_{l\kappa}^\alpha = 0$ [1]. In the molecular field approximation (MFA), one gets the following equation for σ_κ

$$\sigma_\kappa = \mathrm{th}\left\{\frac{1}{\Theta}\sum_{\kappa_1}\left[\left(\frac{A_\kappa A_{\kappa_1}}{B_\kappa B_{\kappa_1}}\right)^{1/2}\Phi^{\kappa\kappa_1}(0)\sigma_{\kappa_1}\right]\right\}. \tag{5.3}$$

There occur significant differences between the results of the standard MFA and of the present model. One of those differences arises from the appearance of $h_\kappa(\Theta)$ in Eq. (5.2) (which does not reach small values for $\Theta \to 0$ contrary to the assumption found in [3]). The other one is the dependence of $J^{\kappa\kappa_1}$ on temperature in UM. The latter causes a significant change in the shape of the curve of $\sigma_\kappa(\Theta)$ when comparing with MFA results, cf. Eq. (5.3) and Ref. [3].

6. *Phase transition in the two-sublattice model*

Let us consider the two-sublattice model, $\kappa = 1, 2$, with additional simplifications

$$M_1 = M_2, \quad A_1 = A_2 \equiv A, \quad B_1 = B_2 \equiv B,$$
$$\Phi_{ll_1}^{11} = \Phi_{ll_1}^{22} \equiv \Phi_{ll_1}.$$

We introduce the dimensionless parameters

$$f_q = \frac{1}{A}\Phi(q), \quad g_q = \frac{1}{A}\Phi^{12}(q),$$
$$\eta_\kappa^\alpha = \left(\frac{A}{B}\right)^{-1/2} x_\kappa^\alpha, \quad y_\kappa^\alpha = \left(\frac{A}{B}\right)^{-1}\langle(u_{l\kappa}^\alpha)^2\rangle, \quad \tau = \frac{\Theta}{(A^2/B)},$$

and assume that $f_0 = f_{q=0} > 0$.

It follows from Eq. (3.2) that in this case the phase transition is of the displacement type, if

(a) $$f_0+g_0 \gtrsim 0.25 \quad \text{for} \quad g_0 > 0, \tag{6.1a}$$

(b) $$2f_0+|g_0| \gtrsim 0.5 \quad \text{for} \quad g_0 < 0. \tag{6.1b}$$

The low-temperature phase can be ferroelectrically (a) or antiferroelectrically (b) ordered. In the high-temperature phase, $\eta_\kappa^\alpha = 0$, one of the optical modes in the system becomes soft. Dynamic instability occurs at the temperature $\tau = \tau_0$, at which the frequency of the soft mode is equal to zero, $\omega_{SM} = 0$. However, the phase transition is of the first order [12, 13]. Therefore, τ_0 is the temperature of instability of the paraelectric phase, the so-called soft mode temperature.

The gap in the soft mode spectrum, Δ, is expressed for $g_0 \gtrless 0$ respectively, as

$$\text{(a)} \qquad \Delta_{g_0>0} = 3[(\eta_1^+)^2+y_1^+]-1 = 3[(\eta_2^+)^2+y_2^+]-1, \tag{6.2a}$$

$$\text{(b)} \qquad \Delta_{g_0<0} = 3[(\eta_1^+)^2+y_1^+]-1+2g_0 = 3[(\eta_2^-)^2+y_2^-]-1+2g_0. \tag{6.2b}$$

It might be seen from Eqs. (6.2) that the gap in the spectrum is caused by a single-particle potential for the ferroelectric phase transition (FPT). For the antiferroelectric phase transition (AFTP), Δ is expressed both by a single-particle potential and the force constant g_0.

From Eqs. (6.2), it results that τ_0 is determined by the following expressions

$$\text{(a)} \qquad \frac{\tau_0}{N}\sum_q \frac{f_0+g_0-f_q}{(f_0+g_0-f_q)^2-g_q^2} = \tfrac{1}{3}, \qquad g_0 > 0,$$

$$\text{(b)} \qquad \frac{\tau_0}{N}\sum_q \frac{f_0+|g_0|-f_q}{(f_0+|g_0|-f_q)^2-g_q^2} = \tfrac{1}{3}(1+2|g_0|), \qquad g_0 < 0.$$

It is expected that the phase transition is of the order-disorder type in a system with the weak interaction between active atoms, $f_0+|g_0| \ll 1$ (see: [3, 14, 15]). Instability of the ordered phase occurs at the temperature τ_K (see: [3])

$$\text{(a)} \qquad \tau_K \simeq f_0+g_0, \qquad g_0 > 0, \tag{6.3a}$$

$$\text{(b)} \qquad \tau_K \simeq f_0+|g_0|, \qquad g_0 < 0. \tag{6.3b}$$

In the case when $g_0 < 0$, the low-temperature phase is antiferroelectrically ordered, as may be seen from Eqs (5.2).

Let us consider the disordered system, $\sigma_1 = \sigma_2 = 0$. The superheating temperature, τ_{sh}, for the phase $\eta_\kappa^\alpha \neq 0$, has a value (for details, see [3]):

$$\text{(a)} \qquad \tau_{sh}(g_0 > 0) \simeq \tfrac{1}{6}[1-2(f_0+g_0)], \tag{6.4a}$$

$$\text{(b)} \qquad \tau_{sh}(g_0 < 0) \simeq \tfrac{1}{6}[1+2(|g_0|-f_0)]. \tag{6.4b}$$

Phase transition of the order-disorder type appears, when instability of the statistical order occurs prior to the dynamic instability

$$\tau_K < \tau_{sh}. \tag{6.5}$$

It follows from Eqs. (6.3–5) that the phase transition in a system is of the order-disorder type when coupling parameters are sufficiently small

$$\text{(a)} \qquad f_0+g_0 \lesssim 0.125, \qquad g_0 > 0, \tag{6.6a}$$

$$\text{(b)} \qquad 2f_0+|g_0| \lesssim 0.25, \qquad g_0 < 0. \tag{6.6b}$$

Phase transition is of the "mixed type" [3], when

$$\eta = 0, \quad \sigma = 0 \quad \text{for} \quad \tau > \tau_c$$

and

$$\eta \neq 0, \quad \sigma \neq 0 \quad \text{for} \quad \tau < \tau_c,$$

where τ_c is the transition temperature. It follows from (6.2) and (6.6) that in our case phase transition is of the mixed type if coupling parameters are in the following regions

(a) $$0.125 \lesssim f_0 + g_0 \lesssim 0.25, \tag{6.7a}$$

(b) $$0.25 \lesssim 2f_0 + |g_0| \lesssim 0.5, \tag{6.7b}$$

When $g_0 > 0$ the above results coincide with those obtained in [3]. This is anyhow evident from the condition $f_0^{(1)} = f_0^{(2)} > 0$.

The discussion of the somewhat more general model, $f_q^{(1)} \neq f_q^{(2)}$ is more complicated. However, the occurrence of different type phase transitions is expected within each of the sublattices. This assumption may contribute to a better understanding of phase transitions in complex structures.

7. *Electric susceptibility*

In this section we discuss the behaviour of the electric susceptibility of the model described in the previous section. It is assumed that all the active atoms carry equal effective charges $e_1 = e_2 \equiv e$.

The fact that the phase transition of order-disorder type is of the second order is not obvious (contrary to [3]), because of appearance of $h_\kappa(\Theta)$ (Eq. (5.2)). This is because we are mostly interested in the temperature dependence of electric susceptibility for such phase transitions. We consider the model with the additional condition $f_0 + |g_0| \ll 1$.

The electric susceptibility $\chi = \left.\frac{\partial P}{\partial E}\right|_{E=0}$ is calculated by taking the derivative of the spontaneous polarization P [3]

$$P = \frac{1}{Nv} \sum_{l\kappa\alpha} \langle \sigma_{l\kappa}^{\alpha} x_{l\kappa}^{\alpha} \rangle \sim \sum_{\kappa} (\sigma_\mu^+ \eta_\kappa^+ + \sigma_\kappa^- \eta_\kappa^-), \tag{7.1}$$

with respect to E. The external field E is introduced as parallel to the atomic displacements, and the Hamiltonian (2.1) is then replaced by

$$H_E = H - \sum_{l\kappa\alpha} eEx_{l\kappa}^{\alpha}. \tag{7.2}$$

In MFA ($\eta_\kappa^\alpha = 1$, $u_{l\kappa}^\alpha = 0$) the susceptibility for FPT ($g_0 > 0$) and AFPT ($g_0 < 0$), respectively, is expressed as

(a) $$\chi_{g_0>0} \sim \begin{cases} \dfrac{1}{\tau - \tau_K}, & \tau > \tau_K = f_0 + g_0 \\[2ex] \dfrac{1}{2(\tau_K - \tau)}, & \tau < \tau_K \end{cases} \tag{7.3a}$$

$$\text{(b)} \qquad \chi_{g_0<0} \sim \begin{cases} \dfrac{1}{2|g_0|+\tau-\tau_{K_1}}, & \tau > \tau_{K_1} = f_0+|g_0|, \\ \dfrac{1}{2|g_0|+2(\tau_{K_1}-\tau)}, & \tau < \tau_{K_1}. \end{cases} \tag{7.3b}$$

These formulae coincide with the results of the phenomenological theory, [16]. In the framework of UM, the atomic vibrations are taken into account, changing the value of the transition temperature. Actually the latter is expressed for $g_0 \gtrless 0$ respectively as

$$\tau_c = (f_0+g_0)\,[1+\gamma(\tau_c)], \tag{7.4b}$$

$$\tau_{c_1} = (f_0+|g_0|)\,[1+\gamma_1(\tau_{c_1})], \tag{7.4b}$$

where

$$\gamma(\tau_c) = \frac{2\eta_0^2(1-\eta_0^2)\,[6\tau_c-(2\eta_0^2)^2]+(f_0+g_0)\,[(2\eta_0^2)^2+3\tau_c]+6\tau_c\eta_0^4}{2\eta_0^2[(2\eta_0^2)^2-6\tau_c]-(f_0+g_0)\,[(2\eta_0^2)^2+3\tau_c]},$$

$$\eta_0^2 = \eta^2(\tau = \tau_c),$$

γ_1 may be obtained from γ by changing

$$g_0 \to |g_0|, \qquad \tau_c \to \tau_{c_1}.$$

Formula for the susceptibility in FPT is of a similar form to that of MFA

$$\chi_{g_0>0} \sim |\tau-\tau_c|^{-1}, \tag{7.5a}$$

i.e. it has a singularity at the transition temperature. Susceptibility for AFPT is a continuous function of temperature

$$\chi_{g_0<0} \sim \begin{cases} [A_1+A_2(\tau-\tau_{c_1})]^{-1} & \tau > \tau_{c_1} \\ [A_1+A_3(\tau_{c_1}-\tau)]^{-1}, & \tau < \tau_{c_1} \end{cases} \tag{7.5b}$$

where A_1, A_2, A_3 are dimensionless constants.

The lattice vibrations lead to the renormalization of the transition temperature. However, they do not change the behaviour of the susceptibility, and so the type of phase transition. Therefore, the Curie–Weiss law for susceptibility is also obtained (Eqs. (7.5)).

8. *Final remarks*

In this paper we have derived the basic equations of UM extended to a case of many active atoms. A wide variety of the possible phase transitions in the two-sublattice model were pointed out. We have derived the criteria of dependence of the transitions' type on coupling parameters f_0 and g_0. It has become evident that the low-temperature phase might be ferro- or antiferroelectrically ordered.

In the case of strongly interacting atoms, the phase transition is of the first order. The soft mode temperature was expressed by the model parameters. In both cases, $g_0 \gtrless 0$, the soft mode appeared for the wave vector $\boldsymbol{q} = 0$. In our model AFPT as well FPT take place without change in translational symmetry.

Phase transition in a system of weakly interacting atoms is of the second order. This fact was established in a discussion of electric susceptibility. In this case the results obtained within UM are qualitatively similar to those of the phenomenological theory.

Finally, let us remark that the present model can be applied to describe the phase transition in some ferroelectric crystals, (e.g. TGS, Rochelle salt). This problem will be discussed elsewhere.

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REFERENCES

[1] V. G. Vaks, *Introduction to Microscopic Theory of Ferroelectrics*, Nauka, Moscow 1973 (in Russian).
[2] A. D. Bruce, K. A. Muller, W. Berlinger, *Phys. Rev. Lett.* **42**, 185 (1979).
[3] S. Stamenkovic, N. M. Plakida, V. L. Aksenov, T. Siklos, *Phys. Rev.* **B14**, 5080 (1976).
[4] G. M. Zaslavsky, V. F. Shabanov, K. S. Aleksandrov, J. P. Aleksandrova, *Zh. Eksp. Theor. Fiz.* **72**, 602 (1977).
[5] K. S. Aleksandrov, J. P. Aleksandrova, G. M. Zaslavsky, V. F. Shabanov, *Zh. Eksp. Theor. Fiz. Pis'ma* **21**, 58 (1975).
[6] K. K. Kobayashi, *J. Phys. Soc. Jpn.* **24**, 497 (1968).
[7] N. M. Plakida, V. L. Aksenov, J. M. Kowalski, V. B. Priezzhev, H. Braeter, *Fiz. Tverd. Tela* **18**, 2920 (1976).
[8] N. M. Plakida, T. Siklos, *Phys. Status Solidi* **33**, 103 (1969); **39**, 171 (1970).
[9] S. V. Tyablikov, *Methods of Quantum Theory of Magnetism*, Nauka, Moscow 1975 (in Russian), p. 195.
[10] N. M. Plakida, *Phys. Lett.* **A32**, 134 (1970).
[11] N. Boccara, *Phys. Status Solidi* b **43**, K11 (1974).
[12] N. S. Gillis, T. R. Koehler, *Phys. Rev.* **B9**, 3806 (1974).
[13] A. J. Sokolov, *Fiz. Tverd. Tela* **16**, 733 (1974).
[14] T. Schneider, E. Stoll, *Phys. Rev.* **B10**, 2001 (1974).
[15] E. Eisenriegler, *Phys. Rev.* **B9**, 1029 (1974).
[16] K. Okada, *J. Phys. Soc. Jpn.* **27**, 420 (1969).