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ABSTRACT

The unified model theory describing both the "order-disorder" and displacive" ferroelectric phase transitions is investigated by introducing the model pseudospin-phonon Hamiltonian. In the second part using the concept of local normal coordinates the tunnelling is also taken into account. On the basis of the self-consistent phonon-field and molecular-field approximations a complete system of self-consistent equations for two order parameters (average displacement of active atoms and average population of atomic equilibrium positions) is obtained. The qualitative discussion as well as the numerical analysis show that the ferroelectric phase transition (first or second order) can be either the order-disorder, displacive, or mixed type, depending on the dimensionless coupling energy between the atoms in the model Hamiltonian.

АННОТАЦИЯ

Предложена обобщенная модель для описания сегнетоэлектрических фазовых переходов как типа "порядок-беспорядок", так и типа "смещения". Во второй части эффекты, связанные с туннелированием, также учтены. На основе приближений самосогласованного фононного поля и молекулярного поля получена самосогласованная система уравнений для двух параметров порядка /среднего смещения активных атомов и средней заселенности их равновесных положений/. Качественный анализ и также нумерическое решение уравнений показывают, что сегнетоэлектрический фазовый переход /первого или второго рода/ может быть как типа порядок-беспорядок, типа смещения, так и смешанного типа в зависимости от величины безразмерной энергии связи атомов в модельном гамильтониане.

KIVONAT

A ferroelektromos fázisátalakulások tárgyalására egy általánositott modellt javaslunk, amely egyaránt jól leirja a rend-rendezetlen tipusu és a rácstorzulással járó fázisátalakulásokat. A tanulmány második részében az állapotok közötti alagutazással kapcsolatos effektusokat is figyelembe vesszük. A self-consistent fonon-tér és molekuláris tér közelitéseket alkalmazva a két rend-paraméter - az aktiv atomok átlagos elmozdulása és egyensulyi helyzeteik átlagos betöltöttsége - meghatározására egy self-consistent egyenletrendszert nyerünk. Az egyenletrendszer kvalitativ vizsgálatából, éppugy mint a numerikus számitások eredményeiből láthatjuk, hogy az atomok redukált kötési energiájától függően lehet ferroelektromos fázisátalakulás első-, illetve másodrendü és rend-rendezetlen tipusu rácstorzulással járó, vagy kevert tipusu.

1. INTRODUCTION

It is generally assumed that there are two basic kinds
of phase transitions in ferroelectrics, one being the
"order-disorder" type and the other being the "displacive"
type (see, for instance, [1]). In the former case the phase
transition results from a statistical disorder of active
atoms among several (in the simplest case, two) equilibrium
positions, as determined for each cell by the remaining atoms.
In the latter case the phase transition is caused by lattice
instability against a certain atomic vibrational mode. Never-
theless, it has been shown in the last several years that both
types of ferroelectric phase transitions can be described
within a single model and that there are not essential diffe-
rences between them [2] - [7] . In the simplest case this
model is described by the Hamiltonian which is expressed as a
sum of single-particle energies, as determined by double-
-minimum potential wells, and the harmonic couplings between
active atoms in different cells. Then the character of the phase
transition depends on the ratio of the harmonic coupling
strength and the height of the single-particle potential barrier.
The nature of the phase transition described by such models
was examined approximately by applying both the Curie-Weiss

molecular-field method and the self-consistent phonon-field method [2] - [8] . It was shown [7] by comparing the results of both methods that for a weak lattice coupling the character of the phase transition is closer to the order-disorder type, which is more consistently described by the molecular--field approximation; for a strong lattice coupling the phase transition has to be related to the displacive type, which can be reasonably described by the self-consistent phonon-field approximation. Such a consistent description can be understood under the circumstances that in the order-disorder transition statistical fluctuations of active atoms onto their equivalent equilibrium position play the main role, which is accurately enough described by the pseudospin model [1] , [9] - [15], while in the displacive transition the dynamical correlations of atomic displacements turn out to be more essential, so the self-consistent phonon-field approximation is more efficient.

However, for a complete description of the ferroelectric phase transition one has to take into account both mechanisms simultaneously in the frame of an universal model. Note, that such a physical concept is essentially different from that con-tained in the model where the pseudospin-lattice interaction is introduced so as to comprise more adequately the dynamics of hydrogen-bonded ferroelectrics [13] - [15] .

In the present lecture a general model for ferroelectric phase transitions [16] , [17] is discussed by introducing two order parameters associated with the motion of active atoms:

the average population $\sigma_\alpha(T)$ for one of two equilibrium positions ($\alpha = +, -$), as determined by the pseudospin approach, and the average displacement $\eta_\alpha(T)$ with respect to the center of the cell, which is determined by the self-consistent phonon scheme. As a consequence, the ferroelectric phase transition can be either of the order-disorder type, when $\sigma_+(T_c) = \sigma_-(T_c)$, or of displacive type, when $\eta_+(T_c) = \eta_-(T_c) = 0$, but it can also have a mixed character, depending on the relations between energy parameters introduced in the model (Section 2 - 7).

However, in the first part of this lecture the single--particle tunnelling motion of active atoms has not been explicitly taken into account. The incorporation of the tunnelling motion as an additional degree of freedom leads to collective excitations which may have a soft mode character [11] or cause the appearance of a central peak [18], [19]. Since the tunnelling energies (of the order of the ground state quantum splitting) are usually much smaller than the characteristic phonon energies, the role of such excitations is predominant at low temperatures ($\Omega \sim k_B T$). On the other hand in addition to a renormalization of the pseudospin-energy parameters of the De Gennes type [9], the higher phonon excitations can lead to the structural phase transition of the displacive type (against a certain vibrational mode) at higher temperatures. So, in the second part of this lecture we take into account self-consistently (within the variation approach of Bogolyubov [20]) the excitations of both types (displacive and order-disorder) - so as to

comprise both the tunnelling and the higher phonon oscillations of active atoms in the frame of a hybridized pseudospin-phonon model Hamiltonian, separated in corresponding variables. This is achieved by representing the cooperative atomic motion as a slow tunnelling process among several (in the simplest case, two) equilibrium positions in addition to familiar phonon-like oscillations around some momentary rest position [21] . On the basis of the self-consistent phonon-field and the molecular field approximations a complete system of coupled equations for two order parameters (average displacement $\eta \sim r_{sa}$, and average localization σ_z) is obtained. A qualitative discussion as well as a detailed numerical analysis [21] , [22] show that the ferroelectric phase transition (of first or second order) can be either of the order-disorder, or of the displacive or of the mixed type, depending predominantly on the ratio of the two--particle potential to the single-particle one and, in a lesser degree, on the ratio of zero-point vibrational energy to the height of the single-particle potential barrier. The possible structural phase transition of both types at zeroth temperature (quantum limit) is also discussed (Section 8 - 11).

2. MODEL HAMILTONIAN

It is usually possible in describing ferroelectric phase transitions to separate a group of atoms whose character of motion depens essentially on temperature, so that one could attribute them to the occurrence of the phase transition. In doing so the action of remaining atoms is replaced by an average

static field, to a first approximation at least. Therefore we
shall consider a simple model where only the motion of active
atoms is taken into account:

$$H = \sum_i \left(\frac{\vec{P}_i^2}{2m} + V(\vec{R}_i) \right) + \frac{1}{2} \sum_{i \neq j} \Phi(\vec{R}_i - \vec{R}_j) \quad . \tag{2.1}$$

Here $\vec{P}_i$ and $\vec{R}_i$ designate the momentum and coordinate referring
to the active atoms, and $V(\vec{R}_i)$ is a single-particle potential
coming from remaining atoms, whereas $\Phi(\vec{R}_i - \vec{R}_j)$ is the potential
of the pair interaction between active atoms in different cells.
P_i and R_i can be also considered as local normal mode coordinates,
describing the critical dynamics (see [1], [30]), as in Section 8.

The potential $V(\vec{R}_i)$ may have two or more minima which pro-
vide the possibility of occupying for active atoms those states
in the cell. For simplicity, let us assume that there are only
two states in each cell, so the atomic coordinate may be repre-
sented (below the transition temperature) as follows:

$$\vec{R}_i = \vec{\ell}_i + \sigma_i^+ \vec{S}_i^+ + \sigma_i^- \vec{S}_i^- \quad , \tag{2.2}$$

Here $\vec{\ell}_i$ designates the center of the cell, and $\sigma_i^+ = 1$ or 0
and $\sigma_i^- = 1 - \sigma_i^+ = 0$ or 1, according to whether the atom
occupies the $+$ or $-$ state, respectively. The projection ope-
rator itself can be expressed by the pseudospin operator

$$\sigma_i^\alpha = \frac{1}{2}(1 + \alpha\sigma_i) \quad , \tag{2.3}$$

which is introduced as an independent variable, commuting with

the atomic displacement ($\vec{S}_i^\alpha$) and momentum $\vec{P}_i^\alpha$ operators. To elucidate such additional pseudospin degree of freedom one has take explicitly account of tunnelling effect being described by x-component of the pseudospin operator [23].

The atomic displacement in the state α, $\vec{S}_i^\alpha$, can be written as a sum of a static displacement $\vec{b}_i^\alpha$ and a thermal fluctuation $\vec{u}_i^\alpha$,

$$\vec{S}_i^\alpha = \vec{b}_i^\alpha + \vec{u}_i^\alpha ; \qquad \vec{b}_i^\alpha = < \vec{S}_i^\alpha > = \vec{b}_\alpha , \qquad (2.4)$$

where the symbol $< \cdots >$ stands for a statistical average with the Hamiltonian (2.1). A generalization and further discussion of the representation (2.2) - (2.4) will be given in Section 8.

Therefore the representation of the atomic coordinate, as given by Eq. (2.2), enables one to take into account, at first, the atomic random distribution over two equilibrium positions in the cell, using the operator σ_i^α, and secondly, the thermal atomic fluctuation $\vec{u}_i^\alpha$ in the neighborhood of a given equilibrium position. In describing order-disorder phase transitions the latter variably are usually neglected, whereas in describing displacive phase transitions it is assumed that all atoms have the identical equilibrium positions in the cells ($\alpha = +$ or $\alpha = -$); thus the operator σ_i^α takes the same value at each site i. In our generalized model we will be able to study

both types of phase transitions using the full representation (2.2). Such a physical picture is in agreement with recent computer simulations and it is also appealing for reason of universality [18]. It should be pointed out that the representation (2.2) for atomic coordinates as a sum of pseudospin and phonon variables was proposed by Vaks and Larkin [47] in their discussion of order-disorder type structural phase transition (see also [1], § 6.). We generalize their representation to consider as well the displacive type phase transition.

Having inserted the expression (2.2) into Hamiltonian (2.1), we can write it as follows:

$$H = \sum_{i,\alpha} \sigma_i^\alpha \left\{ \frac{1}{2m} (\vec{P}_i^\alpha)^2 + V(\vec{\ell}_i + \vec{S}_i^\alpha) \right\} +$$

$$+ \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} \sigma_i^\alpha \sigma_j^\beta \Phi (\vec{\ell}_i - \vec{\ell}_j + \vec{S}_i^\alpha - \vec{S}_j^\beta) \quad .$$

(2.5)

The equilibrium positions of lattice atoms $\vec{b}_\alpha = \langle \vec{S}_i^\alpha \rangle$ are determined using the equilibrium condition in the form

$$i(\partial/\partial t) \langle \vec{P}_i^\alpha (t) \rangle = \langle [\vec{P}_i^\alpha , H] \rangle = 0 \quad ,$$

which leads to the equation

$$\langle \frac{\partial}{\partial \vec{S}_i^\alpha} V(\vec{\ell}_i + \vec{S}_i^\alpha) \rangle +$$

(2.6)

$$+ \sum_{j,\beta} \langle \sigma_j^\beta \frac{\partial}{\partial \vec{S}_i^\alpha} \Phi (\vec{\ell}_i - \vec{\ell}_j + \vec{S}_i^\alpha - \vec{S}_j^\beta) \rangle = 0 \quad .$$

Furthermore, since the atomic displacements with respect to the center of the cell are usually small, $|\vec{b}_\alpha| \ll \vec{\ell} \simeq |\vec{\ell}_i - \vec{\ell}_j|$, the potential energy in Eqs. (2.5) and (2.6) can be expanded in terms of displacements as follows

$$V(\vec{\ell}_i + \vec{S}_i^\alpha) = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\vec{S}_i^\alpha \frac{\partial}{\partial \vec{\ell}_i} \right)^n V(\vec{\ell}_i) ,\tag{2.7a}$$

$$\Phi(\vec{\ell}_i - \vec{\ell}_j + \vec{S}_i^\alpha - \vec{S}_j^\beta) = \tag{2.7b}$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left\{ (\vec{S}_i^\alpha - \vec{S}_j^\beta) \frac{\partial}{\partial \vec{\ell}_i} \right\}^n \Phi(\vec{\ell}_i - \vec{\ell}_j) .$$

To the lowest approximation it suffices to keep only the first few terms, thus writing the single-particle potential in the form

$$V(\vec{\ell}_i + \vec{S}_i^\alpha) = V(\vec{\ell}_i) - \frac{1}{2} A(\vec{S}_i^\alpha)^2 + \frac{1}{4} B(\vec{S}_i^\alpha)^4 ,\tag{2.8}$$

where the parameters A and B define, respectively, the height of the potential barrier $U_o = A^2/4B$ and the distance between the two minima $2S_o = 2(A/B)^{1/2}$.

It is sufficient to take into account only the harmonic terms in the pair interaction (2.7) ,

$$\Phi(\vec{\ell}_i - \vec{\ell}_j + \vec{S}_i^\alpha - \vec{S}_j^\beta) = \Phi(\vec{\ell}_i - \vec{\ell}_j) + \Phi''_{ij} \frac{1}{2} (\vec{S}_i^\alpha - \vec{S}_j^\beta)^2 \qquad (2.9)$$

by taking $\Phi'(\vec{\ell}_i - \vec{\ell}_j) = 0$. Moreover, in agreement with [5] and [7] we will assume that atomic displacements are experienced along a given crystal axis (a one-component order parameter), although the full spectrum of optical lattice vibrations is referred to a three-dimensional case. The part of the Hamiltonian (2.5) which depends on atomic displacements in the present approximation takes the form

$$H = \sum_{i,\alpha} \sigma_i^\alpha \left\{ \frac{1}{2m} (\vec{P}_i^\alpha)^2 - \frac{A}{2} (\vec{S}_i^\alpha)^2 + \frac{B}{4} (\vec{S}_i^\alpha)^4 \right\} +$$

$$\qquad (2.10)$$

$$+ \frac{1}{2} \sum_{\substack{i,j \\ \alpha,\beta}} \sigma_i^\alpha \sigma_j^\beta \Phi''_{ij} \frac{1}{2} (\vec{S}_i^\alpha - \vec{S}_j^\beta)^2 .$$

The equilibrium conditions (2.6) for this Hamiltonian, using the molecular-field approximation for the pseudospin sub-system and assuming its independence of the phonon subsystem

$$\sum_\beta < \sigma_j^\beta (\vec{S}_i^\alpha - \vec{S}_j^\beta) > \simeq < \vec{S}_i^\alpha > - \sum_\beta \sigma_\beta < \vec{S}_j^\beta > = (\vec{b}_\alpha - \vec{b}_{-\alpha}) \sigma_{-\alpha} ,$$

may be written in the form

$$A\vec{b}_\alpha + B < (\vec{S}_i^\alpha)^3 > + (\vec{b}_\alpha - \vec{b}_{-\alpha}) \, \sigma_{-\alpha} \sum_j \phi_{ij}'' = 0 \; . \qquad (2.6a)$$

Having chosen the positive direction of the displacements along the axis $\vec{b}_+$ and using the approximation

$$< (\vec{S}_i^\alpha)^3 > \simeq \vec{b}_\alpha^3 + 3\vec{b}_\alpha < (\vec{u}_i^\alpha)^2 > \; ,$$

the equilibrium conditions may be represented by

$$\eta_\alpha^3 - (1 - 3 \, y_\alpha) \, \eta_\alpha + (\eta_+ + \eta_-) \, f_o \, \sigma_{-\alpha} = 0 \; . \qquad (2.11)$$

Here the dimensionless quantities are introduced

$$\eta_\alpha^2 = (B/A) \, b_\alpha^2 \quad ; \quad y_\alpha = (B/A) < (\vec{u}_i^\alpha)^2 > \; ,$$

$$\qquad (2.12)$$

$$f_{\vec{q}} = \frac{1}{A} \sum_{i \neq j} \phi_{ij}'' \, e^{i\vec{q}(\vec{\ell}_i - \vec{\ell}_j)} \quad ; \quad f_o = f_{\vec{q}=o} \; ,$$

and the average population of the state α ,

$$\sigma_\alpha = < \sigma_i^\alpha > = \frac{1}{2} \, (1 + \alpha\sigma) \quad , \qquad (2.13)$$

in the agreement with the expression (2.3).

The analysis of the equilibrium conditions (2.11) shows that in addition to the zero solution $\eta_+ = \eta_- = 0$, corresponding to the paraelectric phase, the solutions $\eta_\alpha \neq 0$ also are possible. In the case of small values, $f_o \ll 1$, there can exist two equilibrium positions, the magnitudes of which are close to one another $(\eta_+ - \eta_- \simeq \sigma f_o \ll 1)$, and there also exists the solution $\sigma = 0$, corresponding to complete disorder for an order-disorder phase transition. For values of the coupling parameter $f_o \gtrsim 0,25$, only one nonzero solution can exist at all temperatures, for example, $\eta_+ \neq 0$ (for complete atomic order, $\sigma = + 1$). In this region of the coupling parameter only a displacive phase transition is possible.

3. PHONON SUBSYSTEM

Let us determine the phonon spectrum and average values of the atomic displacement correlation functions using the Green's--function method developed in the theory of strongly anharmonic crystals [24] , [25] . Consider a displacement-operator Green's function of general type

$$D_{ij} (t-t') = \ll \vec{u}_i (t) ; \vec{u}_j (t') \gg =$$

$$= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega(t-t')} D_{ij}(\omega) ,$$

(3.1)

where ordinary notation is used. The above Green's function describes the atomic displacement correlations at the lattice sites

i and j, in arbitrary states, because here it is $u_i = \sigma_i^+ u_i^+ +$
$+ \sigma_i^- u_i^-$. Let us also introduce the Green's function for a fixed
atomic state α at the site i by inserting $\sigma_i^\alpha = 1$:

$$D_{i(\alpha),j}(t-t') = \ll \vec{u}_i^\alpha(t) ; \vec{u}_j(t') \gg \quad , \qquad (3.2)$$

which is necessary for the definition of an average quadratic
atomic displacement in the state α ,

$$< (\vec{u}_i^\alpha)^2 > = \int\limits_0^\infty d\omega \coth \frac{\omega}{2k_B T} (-\frac{1}{\pi} \text{Im } D_{i(\alpha),i}(\omega + i\varepsilon)) \quad . \qquad (3.3)$$

Taking into account that the Green's functions (3.1) and (3.2)
contain the statistical average with the full Hamiltonian (2.10),
thus including also the average over all atomic states, and since
those functions depend only on the difference between the atomic
coordinates $\vec{S}_i - \vec{S}_j \simeq \vec{\ell}_i - \vec{\ell}_j$, we will write their Fourier
expansion in terms of the reciprocal lattice vectors $\vec{q}$ as
follows:

$$D_{i(\omega),j}(\omega) = \frac{1}{NA} \sum_{\vec{q}} e^{i\vec{q}(\vec{\ell}_i - \vec{\ell}_j)} D_{\vec{q}}^\alpha(\omega) \quad . \qquad (3.4)$$

The equation of motion for the Green's function (3.2), using
Hamiltonian (2.10), has the form

$$- m \frac{d^2}{dt^2} D_{i(\alpha),j}(t-t') = \delta_{ij} \delta(t-t') -$$

$$- (A - \sum_k \Phi_{ik}'') << \vec{S}_i^\alpha ; \vec{u}_j(t') >> + B << (\vec{S}_i^\alpha)^3 ; \vec{u}_j(t') >> - \qquad (3.5)$$

$$- \sum_{k\gamma} \Phi_{ik}'' << \sigma_k^\gamma \vec{S}_k^\gamma ; \vec{u}_j(t') >> .$$

The Green's function $<< \sigma_k^\gamma \vec{S}_k^\gamma ; \vec{u}_j(t') >>$ on the right-hand side, describes the correlation of atomic displacements at sites k and j under the condition that the atom at the site i is in the state α [$\sigma_i^\alpha = 1$ in Eq. (3.5)]. However, since $k \neq i$ in the sum (3.5), it is possible to neglect the correlation between the states α and γ for atoms at sites k and i, thus annihilating the latter condition, i.e., it is possible to use the molecular-field approximation for the pseudospin subsystem. In addition, having used the approximation of independence between the phonon and pseudospin subsystems, we obtain for the present Green's function the following relation:

$$<< \sigma_k^\gamma \vec{S}_k^\gamma ; \vec{u}_j >> \Big|_{\sigma_i^\alpha = 1} \simeq << \sigma_k^\gamma \vec{S}_k^\gamma ; \vec{u}_j >> \simeq$$

$$\qquad (3.6)$$

$$\simeq < \sigma_k^\gamma > << \vec{S}_k^\gamma ; \vec{u}_j >> .$$

Now having inserted $\vec{S}_i^\alpha = \vec{b}_\alpha + \vec{u}_i^\alpha$ in the Green's function and using the renormalized harmonic approximation [24], [25],

$$<< (\vec{u}_i^\alpha)^3 ; \vec{u}_j >> \simeq 3 < (\vec{u}_i^\alpha)^2 > << \vec{u}_i^\alpha ; \vec{u}_j >> \qquad (3.7)$$

for the Fourier component of the Green's function in Eq. (3.5), one obtains

$$\{ m \omega^2 + A(1-f_o) - 3 B [\vec{b}_\alpha^2 + < (\vec{u}_i^\alpha)^2 >]\}D_{i(\alpha),j}(\omega) =$$

$$\qquad (3.8)$$

$$= \delta_{ij} - \sum_{k,\gamma} \Phi_{ik}'' \sigma_\gamma D_{k(\gamma),j}(\omega) \; .$$

We can use the expressions (3.4) and relations (2.12) to solve the above equation, so the Green's function (3.2) becomes:

$$D_{\vec{q}}^\alpha (\nu) = \frac{\nu^2 - \nu_{-\alpha}^2}{(\nu^2 + \nu_{\vec{q}+}^2) \; (\nu^2 - \nu_{\vec{q}-}^2) - \sigma_+ \sigma_- f_{\vec{q}}^2} =$$

$$\qquad (3.9)$$

$$= \frac{\nu^2 - \nu_{-\alpha}^2}{(\nu^2 - \nu_{\vec{q}1}^2) \; (\nu^2 - \nu_{\vec{q}2}^2)} \; ,$$

where we introduced reduced frequencies

$$\nu^2 = \omega^2 / (A/M) \; ; \; \nu_\alpha^2 = \Delta_\alpha^2 + f_o \; ; \; \nu_{\vec{q}\alpha}^2 = \nu_\alpha^2 - \sigma_\alpha f_{\vec{q}} \; . \qquad (3.10)$$

The gap appearing in the phonon spectrum Δ_α is determined by the Eq.:

$$\Delta_\alpha^2 = 3(\eta_\alpha^2 + y_\alpha) - 1 \; , \qquad (3.11)$$

whereas the phonon frequencies $\nu_{\vec{q}(+,-)}$ in expression (3.9) correspond to atomic vibrations in „right-hand"(+) or „left--hand" (-) equilibrium positions.

If disorder is present in the system, the phonon spectrum as determined by the Green's function poles has two branches,

$$\nu_{\vec{q}}^2(1,2) = \frac{1}{2} (\nu_{\vec{q}+}^2 + \nu_{\vec{q}-}^2) \pm$$

$$\pm \frac{1}{2} [(\nu_{\vec{q}+}^2 - \nu_{\vec{q}-}^2)^2 + (1 - \sigma^2) f_{\vec{q}}^2]^{\frac{1}{2}} \ . \tag{3.12}$$

However, in a limiting case of a complete order, for instance, $\sigma^+ = 1$ and $\sigma^- = o$, Green's function (3.9) becomes

$$D_{\vec{q}}^+ (\nu) = [\nu^2 - (\Delta_+^2 + f_o - f_{\vec{q}})]^{-1} \ , \tag{3.13}$$

thus having only one pole, which corresponds to the vibrations of all atoms in the „right-hand" positions. For $\sigma = o$ the number of atoms in both states becomes equal to each other, $\sigma_+ = \sigma_- = \frac{1}{2}$, so an average field at each site takes the same value: $\Delta_+^2 = = \Delta_-^2 = \Delta_o^2$. Therefore the phonon spectrum in this case is also determined by a single frequency being the pole of the following Green's function:

$$D_{\vec{q}}^{\alpha} (\nu) = [\nu^2 - (\Delta_o^2 + f_o - f_{\vec{q}})]^{-1} \ . \tag{3.14}$$

Hence in both cases the soft mode emerges when the single-
-particle gap (3.11) vanishes, $\Delta_\alpha^2 \to 0$.

The Green's function of general type (3.1) which can be
obtained from Eq. (3.9), using the approximation (3.6), evidently
has the same properties.

The self-consistent equation for the phonon subsystem can be
represented according to Eq. (3.3) in a high-temperature classi-
cal case, in the simple form

$$
\begin{aligned}
y_\alpha &= \frac{B}{A} < (\vec{u}_i^\alpha)^2 > = \\
&= \frac{B}{NA^2} \sum_{\vec{q}} \int_0^\infty d\omega \ \coth \frac{\omega}{2k_B T} \left\{ -\frac{1}{\pi} \operatorname{Im} D_{\vec{q}}^\alpha (\omega + i\epsilon) \right\} \simeq \\
&\simeq \frac{\tau}{N} \sum_{\vec{q}} \int_{-\infty}^\infty \frac{d\nu}{\nu} \left\{ -\frac{1}{\pi} \operatorname{Im} D_{\vec{q}}^\alpha (\nu + i\epsilon) \right\} = \\
&= -\frac{\tau}{N} \sum_{\vec{q}} \operatorname{Re} D_{\vec{q}}^\alpha (0 + i\epsilon) = \frac{\tau}{N} \sum_{\vec{q}} \frac{\nu_{-\alpha}^2}{\nu_{\vec{q}1}^2 \ \nu_{\vec{q}2}^2}
\end{aligned}
$$

(3.15)

where

$$
\tau = \frac{k_B T}{(A^2/B)}
$$

is the reduced temperature.

It is convenient to pass from the summation over vectors $\vec{q}$
in the first Brillouin zone to the integration over frequencies

by introducing the frequency spectrum density

$$g(\omega^2) = \frac{1}{N} \sum_{\vec{q}} \delta (f_o - f_{\vec{q}} - \omega^2) \ . \tag{3.16}$$

Taking into account the expressions (3.10) and (3.12), Eq. (3.15) can be written in the form

$$Y_\alpha = \tau \int_0^\infty \frac{g(\omega^2) \, d\omega^2}{P + Q \, \omega^2} \, [\, \Delta_{-\alpha} + f_o \,] \ , \tag{3.17}$$

where the following abbrevations are introduced

$$P = \Delta_+^2 \, \Delta_-^2 + f_o \, [\, \Delta_+^2 \, \tfrac{1}{2} \, (1 + \sigma) + \Delta_-^2 \, \tfrac{1}{2} \, (1-\sigma)\,] \ ,$$
$$\tag{3.18}$$
$$Q = f_o + \Delta_+^2 \, \tfrac{1}{2} \, (1-\sigma) + \Delta_-^2 \, \tfrac{1}{2} \, (1 + \sigma) \ .$$

Performing the integration in (3.15) in the case of zero temperature, when $\coth(\omega/2 \, k_B \, T) = 1$, taking into account (3.9) one obtains in the quantum limit

$$Y_\alpha = \frac{\lambda}{N} \sum_{\vec{q}} \frac{1}{2(\nu_{\vec{q}1} + \nu_{\vec{q}2})} \, \{\, 1 + \frac{\Delta_{-\alpha}^2 + f_o}{\nu_{\vec{q}1} \, \nu_{\vec{q}2}} \,\} \ , \tag{3.19}$$

where $\lambda = (A/m)^{\frac{1}{2}}/(A^2/B)$ is the quantum parameter, proportional to the ratio of the energy of zero point fluctuations, $\hbar\omega_o = = \hbar(A/m)^{\frac{1}{2}}$ and the height of the barrier in the one-particle potential well, $U_o = (A^2/4B)$.

Now substituting y_α [Eq. (3.17) or Eq. (3.19)] and Δ_α^2 [Eq. (3.11)] in the equilibrium condition (2.11) we arrive at the self-consistent procedure to determine the order parameter $\eta_\pm$, provided that the order parameter σ has been found independently from the analysis of the pseudospin subsystem.

4. PSEUDOSPIN SUBSYSTEM

In order to consider the pseudospin subsystem it is convenient to rewrite the Hamiltonian (2.5) in terms of operators σ_i (2.3) as follows:

$$H = H_\ell + H_s \quad ,$$

$$\tag{4.1}$$

$$H_s = \sum_i h_i \sigma_i - \frac{1}{2} \sum_{i \neq j} J_{ij} \sigma_i \sigma_j \quad .$$

Here H_ℓ is independent of σ_i , and the single-particle „field" has the form

$$h_i = h_{1i} + h_{2i} = \frac{1}{2} (h_{1i}^+ - h_{1i}^-) + \sum_j B_{ij} \quad , \tag{4.2}$$

$$h_{1i}^\alpha = (1/2m) (\vec{P}_i^\alpha)^2 + V(\vec{\ell}_i + \vec{S}_i^\alpha) \quad , \tag{4.2a}$$

where

$$B_{ij} = \frac{1}{2} (\phi_{ij}^{++} - \phi_{ij}^{--} + \phi_{ij}^{+-} - \phi_{ij}^{-+}) \quad , \tag{4.2b}$$

while the Ising-type exchange energy is defined by

$$J_{ij} = \frac{1}{4} (\phi_{ij}^{+-} + \phi_{ij}^{-+} - \phi_{ij}^{++} - \phi_{ij}^{--}) \quad , \tag{4.3}$$

where

$$\Phi^{\alpha\beta}_{ij} = \Phi \ (\vec{\ell}_i - \vec{\ell}_j + \vec{s}^{\alpha}_i - \vec{s}^{\beta}_j) \quad .$$

To find the average value $\sigma = < \sigma_i >$ we use the Bogolyubov variational method, assuming that the pseudospin subsystem can be described by an effective Hamiltonian which is not explicitly dependent on atomic displacement operators,

$$\tilde{H}_s = \sum_i \tilde{h}_i \ \sigma_i - \frac{1}{2} \sum_{i \neq j} \tilde{J}_{ij} \ \sigma_i \ \sigma_j \quad . \tag{4.4}$$

A similar approximation was used [26] to study the spin-phonon interaction in anharmonic ferromagnetic crystals. In this approximation the effective field $\tilde{h}_i$ and the exchange energy $\tilde{J}_{ij}$ are determined by suitable functions being averaged over lattice vibrations,

$$\tilde{h}_i \ = \ < h_i >_\ell = h_1 + h_2 \ ; \quad \tilde{J}_{ij} = < J_{ij} >_\ell \quad .$$

For the model Hamiltonaian (2.10), taking into account the solution of the Green's function (3.9) and the equality $< (\vec{P}^{\alpha}_i)^2 > \simeq (k_B T)m$, at high temperatures we can write these fields in the form

$$h_1 \ = \ (A^2/4B) \ [\ \frac{1}{6} \ (\Delta^4_+ - \Delta^4_-) - (\eta^4_+ - \eta^4_-)] \quad , \tag{4.5}$$

$$h_2 \ = \ - \ (A^2/4B) \ (1/Q) \ [P(y_+ - y_-) + \tau \ (\Delta^2_+ - \Delta^2_-)] \quad . \tag{4.6}$$

As can be easily seen $\tilde{h} = h_1 + h_2$ plays the role of a mean field caused by thermal atomic vibrations (when $\tau \to 0$, $\tilde{h} \to 0$) which tends to zero if $\sigma \to 0$. The effective exchange energy itself is defined by the equilibrium atomic positions,

$$\tilde{J}_{ij} = (A/4B) \quad \phi''_{ij} (\eta_+ + \eta_-)^2 \quad , \tag{4.7}$$

so that above the structural phase transition, when $\eta_\pm = 0$, $\tilde{J}_{ij}$ becomes zero, leading to the unique solution $\sigma \equiv 0$. Using the molecular-field approximation for the order parameter σ we obtain the following equation:

$$\sigma = \tanh \left(\frac{\tilde{J}\sigma - \tilde{h}}{k_B T} \right) ; \quad \tilde{J} = \sum_j \tilde{J}_{ij} \quad , \tag{4.8}$$

or having accounted for the definitions (4.5) - (4.7), its explicit form becomes

$$\sigma = \tanh \left\{ \frac{1}{4\tau} \left\{ \sigma f_o (\eta_+ + \eta_-)^2 + (\eta_+^4 - \eta_-^4) - \frac{1}{6} (\Delta_+^4 - \Delta_-^4) + \right. \right.$$

$$\left. \left. + \frac{1}{Q} [P(y_+ - y_-) + \tau(\Delta_+^2 - \Delta_-^2)] \right\} \right\} . \tag{4.9}$$

In doing so the system of self-consistent equations for the parameters $\eta_\pm$ [Eq. (2.11)] and σ becomes complete where the quantities $y_\pm$ and $\Delta_\pm^2$ are defined by the suitable function (3.17) and (3.11) respectively.

In the quantum-limit, $T = 0K$, an unique solution, $\sigma = 1$ appears (if $\tilde{I}_{ij} > 0$, $h_i \geq 0$). The effect of tunnelling bet-

ween states $\alpha = + 1$ and $\alpha = - 1$, suggested in [23], makes it possible to generalize the Hamiltonian (2.5) and to introduce in (4.4) the transverse field, $\Omega \sum_i \sigma_i^x$, which in turn may lead to the solution $\sigma \to 0$ in the case $T = 0K$.

In addition, we quote the expression for the spontaneous polarization, which is dependent in the present model not only on the atomic order but also on the atomic equilibrium positions, i.e., it is determined by both order parameters $\eta_\pm$ and σ. In dimensionless quantities, the spontaneous polarization is given by

$$P_s = \frac{1}{N} \sum_i \left(\frac{B}{A}\right)^{\frac{1}{2}} (< \sigma_i^+ S_i^+ > - < \sigma_i^- S_i^- >) =$$

$$\text{(4.10)}$$

$$= \frac{1}{2} (\eta_+ - \eta_-) + \frac{1}{2} \sigma(\eta_+ + \eta_-) .$$

If $\tau = 0$, then it follows that $\sigma = 1$, so the polarization takes its maximum value $P_s = 1$; but if $\sigma \to 0$, then it is clear that $P_s \to 0$.

5. THE CLASSICAL LIMIT OF HIGH TEMPERATURES

In the general case the system of self-consistent equations obtained for the order parameters $\eta_\pm$ and σ can only be solved numerically. Nevertheless, even a quantitative analysis of equations - in limiting cases - enables one to draw some definite general conclusions.

At sufficiently low temperatures, $\tau \ll \tau_s$ (τ_s is the lattice-instability temperature), it is possible to neglect the influence of lattice vibrations on the pseudospin subsystem and cosider only Eq. (4.9), with $\eta_+ \simeq \eta_- = 1$. In this case we have just the well-known Ising model from which the phase transition of the order-disorder type (second order) takes place at temperature $\tau_k = f_o$ [using the molecular-field approximation in Eq. (4.9)]. As we will see later this result holds only if $f_o \ll 1$.

By neglecting the temperature dependence of the parameter $\sigma(\tau)$, hereafter, we consider the limiting cases $\sigma = 1$ and $\sigma = 0$.

If $\sigma = 1$, for the quantity $\Delta_+^2 \equiv \Delta^2(\tau)$, from Eqs. (2.11), (3.11) and (3.17) (in the ferroelectric polarized phase $\eta_+ \equiv \eta \neq 0$), we obtain the following equation

$$\Delta^2 = 2\eta^2 = 2 - 6\tau \int_0^\infty \frac{g(\omega^2)\, d\omega^2}{\Delta^2 + \omega^2} \ . \tag{5.1}$$

The solution of Eq. (5.1) was examined in a number of papers (see, for instance [5], [7] and [8]), where it was shown that if the self-consistent phonon-field approximation is applied, then the phase transition becomes of the first order with two characteristic temperatures, one being the soft-mode temperature τ_c, when $\Delta^2 = 0$, and other being the temperature at which the ferroelectric phase instability occurs (the overheating temperature) τ_s. From Eq. (5.1) for the soft-mode temperature we get the estimate

$$\tau_c^{(1)} = \frac{f_o}{3\mu_{-2}} \quad , \tag{5.2}$$

where the index (1) corresponds to $\sigma = 1$. The constant

$$\mu_{-2} = \int_0^\infty \frac{f_o}{\omega^2} \, g(\omega^2) \, d\omega^2 \equiv < \frac{f_o}{\omega^2} >_\omega \quad ,$$

depending on the type of cubic lattice, is equal to $1.5 - 1.3$. For the second characteristic temperature τ_s, in the case of $f_o \ll 1$, we have

$$\tau_s^{(1)} \simeq \frac{1}{6} (1 + f_o) \quad . \tag{5.3}$$

Note, that the limiting value $\tau_s = \frac{1}{6}$, when $f_o \to 0$, is not related to the phase transition, although it has an entirely defined physical meaning: the average kinetic energy of active atoms at this temperature is equal to the height of the potential barrier: $\frac{3}{2} k_B T_s = A^2/4B$. In the case $f_o \gg 1$ the estimation of the temperature τ_s, using the Debye spectrum model, gives

$$\tau_s^{(1)} \simeq \tau_c^{(1)} (1 + \frac{1}{\omega_D^2}) \simeq \tau_c^{(1)} (1 + \frac{1}{2f_o}) \quad . \tag{5.4}$$

If $\sigma = 0$ for the quantities $\Delta_+^2 = \Delta_-^2 = \Delta_o^2(\tau)$ and $\eta_+^2 = \eta_-^2 \equiv \eta_o^2(\tau)$ the self-consistent equation yield

$$\Delta_o^2 = 2\eta_o^2 - f_o = 2 - 3 f_o - 6\tau \int_0^\infty \frac{g(\omega^2) \, d\omega^2}{\Delta_o^2 + \omega^2} \quad . \tag{5.5}$$

This equation can be solved only if $f_o < \frac{2}{3}$, whereas in the

region $f_o \ll 1$ the phase transition described by this equation has the same type as follows from Eq. (5.1). For the characteristic temperature we get

$$\tau_c^{(o)} = \frac{f_o}{3\mu_{-2}} (1 - \frac{3}{2} f_o) = \tau_c^{(1)} (1 - \frac{3}{2} f_o) \quad , \qquad (5.6)$$

where the index (O) corresponds to $\sigma = 0$. Similarly as in the case of $\sigma = 1$ we get the following estimate for the instability temperature τ_s,

$$\tau_s^{(o)} \simeq \frac{1}{6} (1 - 2 f_o) \quad \text{if} \quad f_o \ll 1 \quad . \qquad (5.7)$$

The estimates obtained show that in the general case of an arbitrary value for the parameter σ the temperature $\tau_c(\sigma)$ falls in the interval within the values (5.2), (5.6), and $\tau_s(\sigma)$ is determined by relations (5.3), (5.4) and (5.7). Besides the large hysteresis value $(\tau_s - \tau_c)/\tau_c \geq 1$ corresponds to small values of f_o : $f_o < 0.2$ for $\sigma = 0$, and $f_o < 0.25$ for $\sigma = 1$; in the case $f_o \gg 1$ the hysteresis value is small, in agreement with the estimates based on Eq. (5.4) and cosistent with [5] , [7] and [8] . It follows from these estimates that the order-disorder phase transition is possible only for small f_o :

$$\tau_k < \tau_s^{(o)} \quad \text{if} \quad f_o < 0.12 \quad , \qquad (5.8)$$

if one estimates $\tau_k \simeq f_o$. At higher values of f_o the lattice instability breaks down the order-disorder phase transition, thus giving rise to the displacive phase transition: $\eta_\pm(\tau \to \tau_s) \to 0$. At values $f_o > 0.25$, in agreement with Eq. (2.11), there is merely one stable atomic equilibrium position at each lattice site, so the displacive phase transition is the only possible type, as described by Eq. (5.1). Consequently, a mixed-type phase transition, as described by all three order parameters $\eta_+(\tau)$, $\eta_-(\tau)$ and $\sigma(\tau)$ may be expected only in the very narrow region

$$0.1 < f_o < 0.25 \quad . \tag{5.9}$$

To confirm these general conclusions, the numerical solution of the self-consistent system of equations was carried out using the Debye model for frequency spectrum (3.16), $g(\omega^2) \sim \omega$, $\omega < \omega_D$, and taking the values of the coupling parameter $f_o = 0.1$, 0.12 and 0.15 . Numerical results for $\sigma(\tau)$ and $\eta_\pm(\tau)$ are presented in Figs. 1-3. It can be observed that the above estimates are in good agreement with the numerical calculations. The temperature dependence of the spontaneous polarization (4.10) for different f_o is shown in Fig. 4. Note, that the region of the order-disorder phase transition ($f_o < 0.1$), as compared to the ordinary Ising model, the spontaneous polarization is decreased more rapidly as temperature is increased due to the temperature dependence of the effective exchange energy:
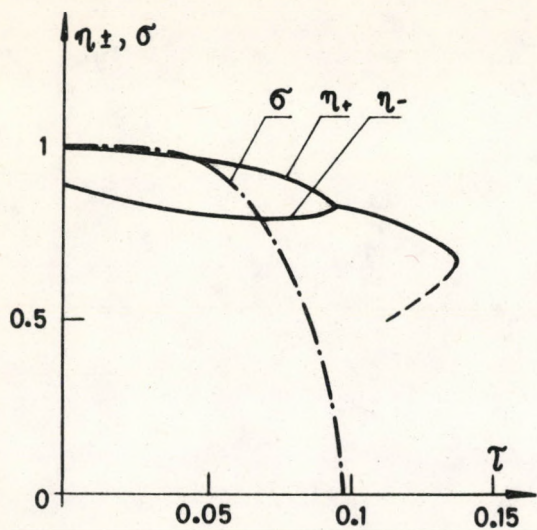$$\tilde{J} = f_o(\eta_+ + \eta_-)^2 \quad .$$

Fig. 1. Temperature dependence of the order parameters: η , average displacement and σ , average pseudospin value for dimension-less coupling parameter $f_o = 0.10$
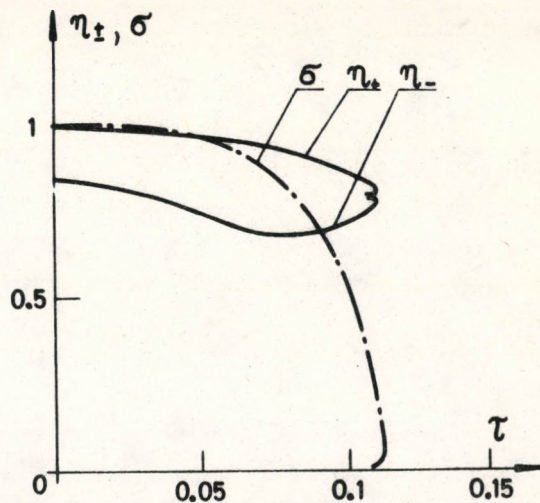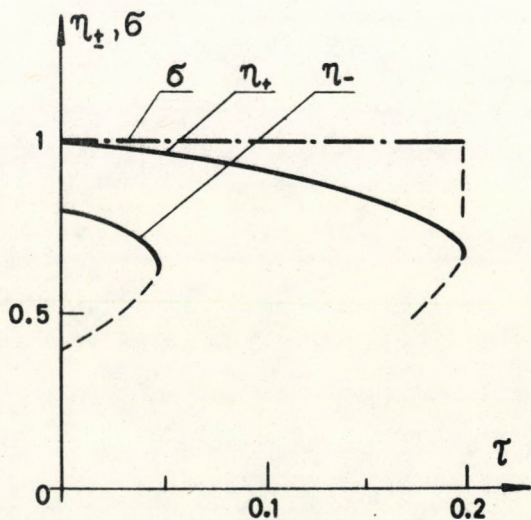

Fig. 2. Same as Fig. 1., for $f_o = 0.12$

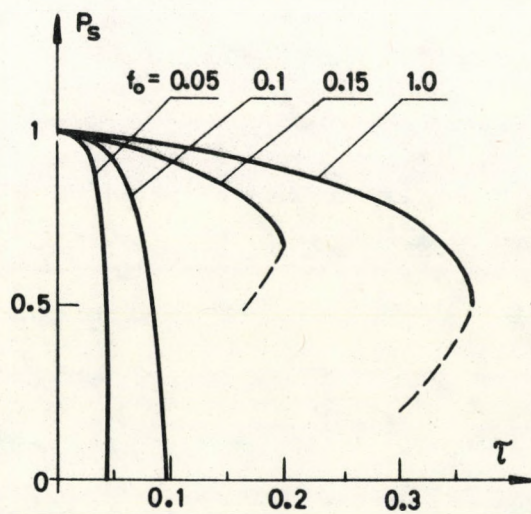Fig. 3. Same as Fig. 1., for $f_o = 0.15$

Fig. 4. Temperature dependence of the reduced polarization P_s for several values of the coupling parameter f_o .

We note, that these features are also obtained by a more sophisticated calculation [27] based on the coherent potential approximation for the disordered lattice.

6. THE QUANTUM LIMIT (T = OK)

In this Section we will investigate only two cases, namely the case of the completely ordered, $\sigma = 1$ lattice and the case of the completely disordered, $\sigma = 0$ lattice [28]. Doing so, we will assume, that the right choise of the value of the transverse field Ω can ensure the transition from $\sigma = 1$ to $\sigma = 0$ in the case of zero temperature: $T = OK$.

a) Displacive type phase transition in ordered lattices.

In the completely ordered lattice all the ions are in the same state, for example $\alpha = +1$ and $\sigma = 1$. In this case the equation of self-consistency (3.19) takes the following form:

$$Y_+ = \frac{\lambda}{2N} \sum_{\vec{q}} \frac{1}{\sqrt{\Delta_+^2 + f_o - f_{\vec{q}}}} = \frac{\lambda}{2} \int_0^{\omega_D} \frac{g(\omega^2)d\omega^2}{\sqrt{\Delta_+^2 + \omega^2}} \quad , \qquad (6.1)$$

where the density of the phonon frequencies (3.16) has been introduced.

Taking into account the condition of equilibrium (2.11), in the case of $\sigma = 1(\sigma_- = 0)$ we obtain one equation for the self-consistent determination of the equilibrium displacement η or the gap in the spectrum of the frequencies $\Delta_+^2 = 2\eta^2$, in

the ferroelectric phase:

$$\eta^2 = 1 - \frac{3}{2} \lambda \int_0^{\omega_D} \frac{g(\omega^2) d\omega^2}{\sqrt{2\eta^2 + \omega^2}} \ . \qquad (6.2)$$

As it can be seen the solution of this equation for the ferroelectric phase with $\eta \neq 0$ exist only if $\lambda < \lambda_{c(1)}$, where the critical value $\lambda_{c(1)}$ is determined by

$$\lambda_{c(1)} = \frac{2}{3} \left\{ \int_0^{\omega_D} \frac{g(\omega^2) d\omega^2}{\omega} \right\}^{-1} = \frac{2}{3} \frac{\sqrt{f_o}}{\mu_{-1}} \ . \qquad (6.3)$$

Here $\mu_{-1} = \overline{\omega^{-1}}$ is the average of the inverse of the frequency; for the Debye spectrum $g(\omega^2) = 3\omega/2\omega_D^3$; $\mu_{-1} = 3/2\sqrt{2} \simeq 1$ if $\omega_D^2 = 2f_o$. Consequently, displacive type transition in ordered lattices can take place only if the lattice consists of sufficiently heavy ions, that is if

$$m > \left(\frac{2}{3} \frac{\sqrt{\varphi_o}}{\mu_{-1}} \frac{A}{B} \right)^{-2} \qquad (6.4)$$

for a given coupling constant φ_o between the ions and a given width $S_o = \sqrt{A/B}$ of the one-particle potential well in accordance with reference [29] .

b) Displacive type phase transition in disordered lattices

Let us discuss the effect of disordering on the displacive type phase transition. Putting in (2.11) and (3.19) $\sigma = 0$, corresponding to equal number of ions in the states $\alpha = +1$ and

$\alpha = -1$ and consequently meaning that $\Delta_+^2 = \Delta_-^2 \equiv \Delta_0^2$, $\eta_+ = \eta_- \equiv \eta$ we get the following system of equations

$$\eta^2 = 1 - f_0 - 3y \quad , \tag{6.5}$$

$$y = \frac{\lambda}{2} \int_0^{\omega_D} \frac{g(\omega^2)\,d\omega^2}{\sqrt{\Delta_0^2 + \omega^2}} \quad . \tag{6.6}$$

Therefore the self-consistent equation for the determination of the gap, $\Delta_0^2 > 0$ in the phonon spectrum in the case of $\sigma = 0$ and $\eta > 0$ takes the following form

$$\Delta_0^2 = 2\eta^2 - f_0 = 2 - 3f_0 - 3\lambda \int_0^{\omega_D} \frac{g(\omega^2)\,d\omega^2}{\sqrt{\Delta_0^2 + \omega^2}} \quad . \tag{6.7}$$

Displacive type phase transition, $\eta > 0$, can take place if $\lambda < \lambda_{c(0)}$, where the critical value of λ is determined by the condition $\Delta_0^2 (\lambda_{c(0)}) = 0$, that is

$$\lambda_{c(0)} = \frac{2}{3} \frac{\sqrt{f_0}}{\mu_{-1}} (1 - \frac{3}{2} f_0) = \lambda_{c(1)} (1 - \frac{3}{2} f_0). \tag{6.8}$$

Consequently, the occurrence of the disordering decreases both the limiting value of the allowed energy of the zero-point fluctuations and the limiting value of the temperature of the phase transition in the classical limit of high temperatures: $\tau_c^{(0)} = \tau_c^{(1)} \{1 - (3/2) f_0 \}$ (5.6). However it has to be mentioned that the transition into the state $\sigma = 0$ can take place only .

if $f_o \ll 1$, and therefore formula (6.8) is valid only if $f_o \ll 1$. In the case $f_o > 1$, only the state with $\sigma = 1$ is possible and formula (6.3) is valid. In this connection it is interesting to note, that by taking into account the possibility of cluster formation in the displacive limit, $f_o \gg 1$, that is equivalent to the introduction of an inhomogeneous order parameter, $\eta = \eta(\vec{r})$, one can also decrease the temperature of phase transition. So one can claim, that the disorder in the equilibrium positions should diminish the temperature of structural phase transition.

7. SOME REMARKS

By comparing our results with those in Refs. [4]-[8] we emphasize an important adventage of the present description method for ferroelectric phase transitions by two order parameters. It enables one to choose various approximations: the molecular-field approximation for the parameter $\eta(T)$ in Eq.(4.9), and the self-consistent phonon-field approximation for η_α and y_α in Eq. (3.17), (3.19), which, in a manner consistent with Refs. [5] and [7], offers a satisfactory description of the phase transition, both in the case $f_o \ll 1$ (order-disorder transition of second order) and in the case $f_o \gg 1$ (the displacive transition for the parameter $\eta(T)$, of first order, close to second order), respectively. It is necessary to point out that the true order of the phase transition (first or second) cannot be predicted in the mean-field approximation (see, for instance, Ref. [1]), so we will not discuss this question (see also Refs. [4], [5] and [8]).

8. THE GENERALISED MODEL HAMILTONIAN

In a model description of the structural phase transition dynamics it is convenient to use the representation of local normal coordinates [30] , [31] involving all active atoms in the given critical mode vibration and to take a simplified model Hamiltonian in the form:

$$H = \sum_i \{ - \frac{\hbar^2 \nabla_i^2}{2m} + U(S_i) \} + \frac{1}{2} \sum_{i \neq j} V(S_i, S_j). \qquad (8.1)$$

Here m is the corresponding residual mass; the single-particle potential $U(S_i)$ and the pair interaction $V(S_i, S_j)$ define the critical dynamics of a given crystal system (N different unit cells are labelled by the index i and their central positions by the vectors $\vec{\ell}_i$).

Our previous coordinate representation $S_i = \sum_\alpha \sigma_{i\alpha}(b_{i\alpha} + u_{i\alpha})$ described the atomic random distribution (within the Ising model - through the projection operator $\sigma_{i\alpha} = \frac{1}{2}(1 + \alpha\sigma_{iz})$), over two (α = +, -) equilibrium positions $(b_{i\alpha})$ as well as the thermal atomic fluctuations $(u_{i\alpha})$ around them ("left" and "right" phonons). However, to elucidate more profoundly such additional pseudo-spin degree of freedom (σ_{iz}), one has to take into account the inherent quantum mechanical effect manifested in a single-particle tunnelling motion of active atoms inside some (real or effective) double-well potential, which was fully missing in our previous

Sections, and rather implicit in the approaches of other authors
(see, for example, the relevant references quoted in Ref. [18]).
For this purpose we suggested [23] the „left-right" represen-
tation of the model Hamiltonian (8.1) in the non-orthogonal
pseudospin basis. However, in accordance with the exhaustive
analysis of Beck [18] the more clear physical picture (and
rather transparent procedure, presented hereafter) can be
introduced by natural generalization of the traditional concept
of atomic equilibrium states. Thus, a time dependent local normal
coordinate may be decomposed into a slow tunnelling-like dis-
placement (r_i) and comparatively fast superimposed deviations
of the phonon type (u_i):

$$S_i = r_i + u_i \; ; \quad < u_i > = 0. \qquad (8.2)$$

Such a representation holds under the „adiabatic" condition
$\Omega << \omega_o$, ω_o being a characteristic frequency of lattice vibra-
tions.

Having inserted the definition (8.2) into the general
Hamiltonian (8.1), it can be written in a trial form, separated
in corresponding variables

$$H_o = H_{ph} (\{ u_i \}) + H_s(\{ r_i \}), \qquad (8.3)$$

where

$$H_{ph} = \sum_i \frac{P_i^2}{2m} + \frac{1}{2} \sum_{ij} \Phi_{ij} u_i u_j , \qquad (8.4)$$

$$H_s = \sum_i \left\{ \frac{p_i^2}{2m} + \tilde{U}(r_i) \right\} + \frac{1}{2} \sum_{i \neq j} C_{ij} (r_i - r_j)^2 , \qquad (8.5)$$

Φ_{ij} , C_{ij} and $\tilde{U}(r_i)$ being the variational parameters and P_i and p_i - the canonical conjugate momenta to u_i and r_i, respectively.

For a strongly anharmonic motion described by Eq. (8.5) it is convenient to introduce the energy representation with respect to the ground doublet symmetric (Ψ_s) and antisymmetric (Ψ_a) single-particle states

$$\left\{ \frac{p_i^2}{2m} + \tilde{U}(r_i) \right\} \Psi_{s,a}(r_i) = \varepsilon_{s,a} \Psi_{s,a}(r_i) , \qquad (8.6)$$

and going over to the pseudospin representation H_s is cast in the well known form of De Gennes [9]

$$H_s = - \Omega \sum_i \sigma_i^x - \frac{1}{2} \sum_i J_{ij} \sigma_i^z \sigma_j^z + E_o , \qquad (8.7)$$

where the energy parameters Ω , J_{ij} and E_o are simple functions of ε_α , C_{ij} and the matrix elements $r_{\alpha\beta} = < \alpha |r_i| \beta >$ and $r_{\alpha\alpha}^2 = < \alpha |r_i^2| \alpha >$ ($\alpha, \beta = s,a$) , calculated with the wave functions in Eq. (8.6):

$$\Omega = \frac{1}{2} (\varepsilon_a - \varepsilon_s) + r_-^2 \, C_o ,$$

$$E_o = \frac{1}{2} (\varepsilon_a + \varepsilon_s) + r_+^2 \, C_o , \qquad (8.8)$$

$$J_{ij} = 2r_{sa}^2 C_{ij} ,$$

$$r_{\pm}^2 = \frac{1}{2} (r_{aa}^2 \pm r_{ss}^2),$$

$$C_o = \sum_j C_{ij} .$$

The variational parameters Φ_{ij}, C_{ij} and $\tilde{U}(r_i)$ are determined from the Bogolyubov variational approach [20], namely from the condition of stationarity of the free energy,

$$F = F_o + < H - H_o >_o \; ; \tag{8.9}$$

where

$$F_o = T \, \ln \, Sp \, \{ e^{- H_o/T} \} \; , \tag{8.10}$$

$$< H - H_o > = Sp \, \{ e^{\frac{F_o - H_o}{T}} (H - H_o) \} =$$

$$= \sum_i < U(r_i + u_i) >_o + \frac{1}{2} \sum_{ij} < V(r_i + u_i \, , \, r_j + u_j) >_o -$$

$$- \sum_i < \tilde{U}(r_i) >_o - \frac{1}{2} \sum_{ij} \Phi_{ij} < u_i u_j >_o - \frac{1}{2} \sum_{ij} C_{ij} <(r_i - r_j)^2 >_o ,$$

$$\tag{8.11}$$

with respect to variations over these parameters or, equivalently, over the corresponding correlation functions, providing $< p_i \, p_i >_o = 0$. For the variational parameters of the trial Hamiltonian (8.4) in the pseudospin representation we obtain the equations:

$$\Phi_{ij} = \frac{\delta}{\delta <u_i \, u_j>_o} \; \{ \; 2 \sum_i \; < U(r_i + u_i) \; >_o \; +$$

$$+ \sum_{i \neq j} \; < V(r_i + u_i \; , \; r_j + u_j \;) \; >_o \; \} \; , \tag{8.12}$$

$$2r^2_{sa} \; C_{ij} = \frac{\delta}{\delta <\sigma^z_i \, \sigma^z_j>_o} \; < V(r_i + u_i \; , \; r_j + u_j) \; >_o \; , \tag{8.13}$$

and

$$\frac{\delta}{\delta <\sigma^x_i>_o} \; \sum_i \; < \tilde{U}(r_i)>_o = \frac{\delta}{\delta <\sigma^x_i>_o} \; \{ \; \sum_i \; < U(r_i + u_i)>_o \; +$$

$$+ \frac{1}{2} \sum_{ij} \; < V(r_i + u_i, \; r_j + u_j)>_o \; - \; \frac{1}{2} \sum_{ij} C_{ij} < r^2_i + r^2_j \; >_o \; \} . \tag{8.14}$$

The self-consistent system of equations (8.4), (8.5), (8.6) (8.12)-(8.14) determines the phase transition of the model and describes the mutual influence of phonon and pseudospin subsystems, if the potentials $U(s_i)$ and $V(s_i, s_j)$ are given.

9. THE STRUCTURAL PHASE TRANSITION IN THE FERROELECTRIC MODEL

Having chosen the single-particle double-well potential in the convenient form (2.8) and the pair potential in Eq (8.1) in the harmonic approximation (2.9); the Hamiltonian takes the form:

$$H = \sum_i \; \{ \; \frac{P^2_i}{2m} \; - \; \frac{A}{2} \; S^2_i \; + \; \frac{B}{4} \; S^4_i \; \} \; + \; \frac{1}{4} \sum_{ij} \varphi_{ij} \; (S_i - S_j)^2 . \tag{9.1}$$

This model was in detail investigated recently (see, for example,

[18],[32]). The variational approach for this Hamiltonian yields:

$$\Phi_{ij} = \delta_{ij} (\Delta + \varphi_o) - \varphi_{ij}(1 - \delta_{ij}) \; ; \quad 2C_{ij} = \varphi_{ij} , \qquad (9.2)$$

where

$$\Delta = - A + 3B(<u_i^2>_o + <r_i^2>_o) \; ; \quad \varphi_o = \sum_j \varphi_{ij} . \qquad (9.3)$$

The effective single-particle potential in (8.5) can be written in form

$$\tilde{U}(r_i) = - \frac{\tilde{A}}{2} r_i^2 + \frac{B}{4} r_i^4 \; ; \quad \tilde{A} = A - 3B <u_i^2>_o . \qquad (9.4)$$

The self-correlation displacement functions relevant for the nature of the structural phase transition are determined by the following approximative equations (of the RPA type)

$$<u_i^2>_o = \frac{1}{Nm} \sum_k \frac{1}{2\omega_k} \coth \frac{\omega_k}{2k_B T} , \qquad (9.5)$$

$$<r_i^2>_o = \frac{1}{2} [(r_{ss}^2 + r_{aa}^2) + (r_{ss}^2 - r_{aa}^2) < \sigma_i^x >], \qquad (9.6)$$

where the phonon frequency is given by the equation

$$m\omega_k^2 = \Delta + \varphi_o - \varphi_k \; ; \quad \varphi_k = \sum_j \varphi_{ij} \, e^{-i\vec{k}(\vec{\ell}_i - \vec{\ell}_j)} . \qquad (9.7)$$

In the mean-field approximation one gets (see, e.g. [1], [33]):

$$< \sigma_i^{x,z} > = \sigma_{x,z} = \frac{h_{x,z}}{h} \, th \, \frac{h}{k_B T} \quad ;$$

$$\tag{9.10}$$

$$h_x = \Omega \quad , \quad h_z = J_o \, \sigma_z \quad , \quad h^2 = h_x^2 + h_z^2 \; .$$

Thus, the structural phase transition is described by the solution of the above self-consistent system of equations for two order parameters (σ_z and r_{sa}) which, owing Eq. (8.6), can be obtained only numerically. Nevertheless a qualitative analysis for the limiting cases is possible.

a) Order-disorder transition

Analogously to the analysis in the previous Sections, in the weak coupling limit, i.e., in the temperature region when

$$\varphi_o \quad \ll \quad \tilde{A} = A - 3B < u_i^2 > \tag{9.11}$$

the order-disorder transition is possible in the pseudospin subsystem through mediation of the order parameter σ_z . In the molecular field approximation for the transition temperature one finds

$$T_c = J_o \, \frac{2q}{\ell n \, \frac{1+q}{1-q}} \qquad ; \qquad q = \Omega/J_o \leqslant 1. \tag{9.12}$$

The estimations obtained in the case of weak tunnelling ($\Omega \ll J_o$; $r_{ss}^2 \sim r_{aa}^2 \sim r_{sa}^2 \sim \tilde{r}_o^2 = \tilde{A}/B$) correspond to the results of the Section 5. (for $f_o \ll 1$, therein), namely

$$T_c \sim J_o \sim \varphi_o \; \tilde{r}_o^2 \sim \varphi_o \; \frac{A}{B} \ll U_o. \tag{9.13}$$

Note, that the phonon excitations do not play an essential role in this case, since $< u_i^2 > \ll \tilde{r}_o^2$.

b) Displacive transition

When the temperature is raised the atomic fluctuations $< u_i^2 >$ can not be neglected and the character of the coupling could be changed, i.e. $\varphi_o \gg \tilde{A}$ (even for $\varphi_o \ll A$), thus leading to the displacive phase transition $[\Delta(T_o) \to 0$ and $\tilde{r}_o^2(T_o) \to 0$; $\tilde{r}_o^2(T_o) = \tilde{A}/B$] . In the classical limit of high temperatures

$$\tilde{A}(T_o) = 0 \; , \quad < u_i^2 > \; = \frac{1}{3} \; \frac{A}{B} \; , \tag{9.14}$$

while in the strong-coupling limit $< u_i^2 > \sim T/m\omega_o^2 \sim T/\varphi_o$ and the transition temperature is estimated as

$$T_o \sim \frac{1}{3} \; \varphi_o \; (A/B). \tag{9.15}$$

A similar result have been obtained in Section 5.

10. THE MODEL AND THE RESULTS OF NUMERICAL CALCULATIONS

For the trial wave functions in Eq. (8.6) with the renormalized $(A \to \tilde{A})$ double-well potential in (9.1), we assume the linear combinations of the ground states of the „left" (-) and „right" (+) unperturbed harmonic oscillators

$$\Psi_{s,a} = \{ 2(1 \pm \rho) \}^{-\frac{1}{2}} [\ \Psi_o^+(r) \pm \Psi_o^-(r) \ ] ; \tag{10.1}$$

$$\Psi^{\pm}(r) = \Psi_o(r \pm \tilde{r}_o) ; \quad \Psi_o(r) = (a\sqrt{\pi})^{-\frac{1}{2}} \exp(-r^2/2a^2) ; \tag{10.2}$$

$$a^2 = 1/m\omega ; \quad \omega^2 = k/m , \quad \tilde{r}_o^2 = (\tilde{A}/B), \ (\hbar = 1) .$$

Here ρ is the overlap and the harmonic force constant is taken to be $k = 2\tilde{A}$ (in the approximation of a strong particle localization). By performing corresponding calculations one finds

$$\rho = \int \Psi^+ (r) \ \psi^-(r) \ dr = \exp \{ - \frac{\tilde{A}^2/B}{\omega/2} \} = \exp(-1/\lambda); \tag{10.3}$$

$$\lambda = \frac{\omega}{2 \ \tilde{A}^2/B} = a^2/\tilde{r}_o^2 = \frac{\lambda_o}{\sqrt{2} \ (1-3 \ y)^{3/2}} , \tag{10.4}$$

where the temperature independent quantum parameter characterizing the zero-point vibrations, $\lambda_o = \omega_o /(A^2/B) ; \quad \omega_o = \sqrt{A/m}$, is introduced and $y = (B/A) < u_i^2 >$ is the reduced average quadratic „fast" displacement, after Eq. (9.5).

Consistently, for the parameters of the pseudospin Hamiltonian (8.7) the following expressions are obtained:

$$\Omega = \frac{A^2}{4\sqrt{2} \ B} \ \frac{\lambda_o \ \rho\sqrt{1-3y}}{(1 - \rho^2)} \ (1 + \frac{3}{\lambda}), \tag{10.5}$$

$$r_{s,a}^2 = \tilde{r}_o^2/(1 - \rho^2) \ ; \quad \tilde{r}_o^2 = (A/B) (1-3y), \tag{10.6}$$

$$r^2_{\substack{ss \\ aa}} = \frac{\tilde{r}^2_o}{1 \pm \rho} \{ 1 + \frac{\lambda}{2} (1 \pm \rho) \}, \tag{10.7}$$

and the reduced average quadratic „slow" displacement (9.6) becomes

$$\bar{r} = \frac{B}{A} < r^2_i > = \frac{1-3y}{1-\rho^2} \{ 1 + \frac{\lambda(1-\rho^2)}{2} - \rho\sigma_x \}. \tag{10.8}$$

To explicit the reduced average quadratic „fast" displacement (9.5), the spectral density of phonon frequencies is introduced,

$$g(\nu) = \frac{2}{\pi} \sqrt{1 - \nu^2} ; \qquad \nu = \frac{\omega}{A/m} , \tag{10.9}$$

so, that

$$y = \lambda_o \int_{-1}^{1} \frac{d\nu \ g(\nu)}{2\sqrt{\Delta - f_o \nu}} \coth \frac{\lambda_o \sqrt{\Delta - f_o \nu}}{2 \theta} , \tag{10.10}$$

$$f_o = \varphi_o/A ; \qquad \theta = \frac{k_B T}{A^2/B}$$

and

$$\Delta = -1 + 3(y + \bar{r}) \tag{10.11}$$

being a gap in the phonon spectrum.

Finally, owing to Eq. (10.6), the spontaneous polarization of the system is simply expressed as

$$P_s = \frac{1}{N} \sum_i (\frac{B}{A})^{\frac{1}{2}} < r_i > = (\frac{B}{A})^{\frac{1}{2}} r_{sa}\sigma_z = \eta \ \sigma_z , \tag{10.12}$$

where

$$\eta = \{ \frac{1 - 3y}{1 - \rho^2} \}^{\frac{1}{2}}. \tag{10.13}$$

Both the „order-disorder" (σ_z) and the „displacive" (η) order parameters have to be found as a self-consistent solution of Eqs. (9.10), (10.3)-(10.11). For a given set of the reduced energy parameters (λ_o, f_o) the competition of these order parameters determines the character of the SPT.

a) The quantum limit of zero temperature.

At zero temperature Eqs. (9.10), (10.10) become

$$\sigma_z = \frac{1}{J_o} \sqrt{J_o^2 - \Omega^2} \quad ; \qquad \sigma_x = \frac{\Omega}{J_o} , \quad \sigma_z \neq 0 \quad ; \tag{10.14}$$

$$y = \lambda_o \int_{-1}^{1} \frac{d\nu \sqrt{1 - \nu^2}}{\pi \sqrt{\Delta - f_o \nu}}. \tag{10.15}$$

As it easily seen from Eq. (10.14), $\sigma_z > 0$ if $\Omega < J_o$. Using Eq. (10.15) one obtains the condition on λ_o

$$\frac{\rho_c}{4f_o} (3 + \lambda_c) (1 - 3y_c) = 1, \tag{10.16}$$

which defines the maximum $\lambda_o(\lambda_c)$ at which $\sigma_z > 0$ is still possible. In a simplified case, when $y_c << \frac{1}{3}$, the graphical solution of Eq. (10.16) gives

$$\lambda_{o,s} \simeq 1/\ell n (3/4 f_o); \tag{10.17}$$

if $\lambda > \lambda_o$, $\sigma_z = 0$ even at zero temperature. The order para-
meter η can also vanish at $T = 0K$. Using Eqs. (10.10), (10.11)
one obtains

$$\lambda_{o,ph} \simeq 2 \sqrt{f_o} . \qquad (10.18)$$

In such a way the zero-point vibrations can destroy the ordered ground
state at $T = 0K$, both in the pseudospin and the phonon sub-
systems. One can expect that P_s vanishes either in σ_z or in η,
depending on the mutual competition between $\lambda_{o,s}$ and $\lambda_{o,ph}$,
i.e. on the lesser of them two. The estimates are given in
Table I.

Table I.

f_o	0.05	0.10	0.50
$\lambda_{o,s}$	0.37	0.50	2.50
$\lambda_{o,ph}$	0.44	0.62	1.40

b) Result of numerical calculations

The system of the self-consistent equations (9.10),(10.3) -
- (10.11) was solved numerically for various f_o and λ_o [21],
[22] . It can be observed that the above estimates are in good
agreement with the numerical calculations.

11. CONCLUDING REMARKS

We have developed a novel approximative scheme which takes
into account simultaneously all the intriguing features of the
structural phase transition, i.e. the statistical order-disorder,
the tunnelling and phonon oscillations in the frame of only one
universal model. Our model description is based on the assumption
that the local normal coordinate can be decomposed into a slow
„tunnelling (hopping) displacement" and a phonon-like one.
In consequence, the energy spectrum of coupled quartic oscilla-
tors is represented as low-lying strong anharmonic excitations
(due to the tunnelling - in distinction from Ref. [18], where
the pseudospin-flip-type motion is associated with the classical
transfer across the barrier) and higher phonon like excitations,
rather weak anharmonic interactions of which being described in
the renormalized harmonic approximation. However, since the
energy spectrum of a particle in a local double-well potential
has quite a complex structure [18] , [34] such a separation has
merely an interpolatory character, i.e. being physically inappli-
cable for a temperature region $k_B T \sim \hbar \Omega \sim \hbar \omega_o$. In particular,
one could expect a more complex renormalization of the pseudo-
spin parameters in real order-disorder compounds, especially
when the excited atomic states lie in the critical temperature
region, $k_B T_c \sim J_o \sim \hbar \omega_o$.

Besides the theoretical and numerical analysis presented,
it should be pointed out that our new model reveals satisfactory

the essential features both the order-disorder and displacive type structural phase transitions at finite and zero temperatures. The true quantummechanical situation, i.e., the tunnelling (local or effective) motion of active atoms is treated properly with respect to the approximations applied and limiting cases considered.

Concluding this lecture, it is our belief that the present model, as analyzed by means of a more accurate self-consistent procedure, in addition to its extension in the spirit of the central peak dynamics [19] and solitary waves [35] , [36] , could complete the analytic description of the critical dynamics and yields deeper insight into the nature of the structural phase transitions in general.

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