

# MAGNETIC AND ELECTRICAL ORDERING OF DIELECTRICS WITHIN THE THEORY OF IONIC AND COVALENT BONDS

A. I. MITSEK

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Institute for Metal Physics, Nat. Acad. Sci. of Ukraine  
(36, Academician Vernadsky Blvd., Kyiv 03142, Ukraine)

The competition of hetero- and homopolar (covalent) bonds and their fluctuations (CBF) is considered as a basis of ferromagnetic ((FM) or antiferromagnetic (AFM)) and ferroelectric (FE) ordering. The exchange integrals of FM and (AFM) signs are calculated in the multielectronic operator spinors (MEOS) representation (for the Heisenberg model). Local FE deformations ( $\hat{\xi}$ ) create electrical polarization  $P(\hat{\xi})$ . The singularities of CBF spectra in the FE phase destabilize it and define  $T_c(\hat{\gamma})$ . The electroelastic coefficients  $\hat{\gamma}$  are the combinations of ionic charges inhomogeneities and bond energies. FE phase diagrams and the types of transitions differ for different values of  $\hat{\gamma}$ .

## 1. Ionic Charges and the MEOS Representation

FM order and FE in dielectrics are united in the section of cooperative phenomena [1]. The thermodynamic theory (or rather, the mean field theory of Stoner (see [2]) or Devonshire (see [3 - 5]) for FM or FE systems) considers these phenomena in the same way near the Curie temperature  $T = T_c$ . It distinguishes dielectrics from FM metals or semiconductors. The applicability of the one-electronic theory to the latter is discussed frequently (see [2] and later reviews, for example, [6]) though without large successes. Whereas FM and FE dielectrics can be calculated only on a multielectronic basis, see [7].

The localization of spins  $\vec{S}_{\vec{r}}$  (or angular moment  $\vec{J}_{\vec{r}}$ ), as well as electrical dipoles, at lattice sites  $\mathbf{r}$  is adequately described by the multielectronic operator spinors (MEOS) [8]. The covalent bonds and their fluctuations (CBF) are taken into account besides heteropolar (ionic) bonds. The wave functions of magnetic cations are separated on core functions ( $\hat{D}_{\vec{r}}^n$  for  $n$  electrons or holes in an unfilled shell) and the function of covalent electron ( $\hat{D}_{\vec{r}}^1$ ). Core and covalent electrons of anions ( $2p$ -electrons in the case of  $O^{2-}$ ) are described by the identical MEOS ( $\hat{P}_{\vec{R}}$ ). We limit ourselves here by  $3d$ -cations. When FM (or antiferromagnetic - AFM) order is calculated,  $n = 2S$ . For FE crystals,  $n = Z$  is the cation charge.

The FM wave function of  $3d-t_{2g}$ -electrons [8, 10] is

$$\hat{D}_{\vec{r}}^n = \{d_{\vec{r}\vec{S}}^n c_{\vec{r}\vec{S}} v_{\vec{r}\vec{L}}\}, \quad d_{\vec{r}\vec{S}}^n = \prod_{\mu=1}^n a_{\vec{r}\mu\sigma}^{\pm},$$

$$S = n\sigma, \quad \sigma = \pm 1/2, \quad (1.1)$$

where  $a_{\vec{r}}^{\pm}$  - the one-electronic Fermi operator. Further the induced orbital polarization is neglected ( $L = 0, v_{\vec{r}\vec{L}} = 1$ ). We consider  $n = 3$  (Fe, Mn, Co, and others with local spin  $S = 3/2$ ). The MEOS spin factor (1.1)

$$c_{\vec{r}\vec{S}}^2 = (1 + \vec{S}\vec{S}_{\vec{r}})/2S + 1, \quad d^+ = \bar{d}, \quad (1.2)$$

is determined in the spin space [2, 8]. The covalent electrons' MEOS is

$$\hat{D}_{\vec{r}}^1 = \{d_{\vec{r}\vec{\sigma}}^1 c_{\vec{r}\vec{\sigma}}\},$$

$$d_{\vec{r}}^n \bar{d}_{\vec{r}}^n = 1, \quad [d_{\vec{r}}^n \bar{d}_{\vec{R}}^m]_+ = \delta_{mn} \delta_{\vec{r}\vec{R}}, \quad N = 1 \text{ or } 3. \quad (1.3)$$

The MEOS spin factor (1.3) is derived similar to (1.2) for  $n = 1$ . Here, polarization is  $\vec{s}_{\vec{r}}$  (instead of  $\vec{S}_{\vec{r}}$  for a magnetic shell).

The charge of an  $O^{2-}$  anion ( $Z = 2$ ) differs from the number of its covalent electrons ( $n = 1$ ). Its MEOS is

$$\hat{P}_{\vec{R}} = \{p_{\vec{R}\vec{\sigma}} c_{\vec{R}\vec{\sigma}}\},$$

$$c_{\vec{r}\vec{\sigma}}^2 = (1 + \vec{\sigma}\vec{\sigma}_{\vec{R}})/2, \quad [p_{\vec{r}} \bar{p}_{\vec{R}}]_+ = \delta_{\vec{r}\vec{R}}. \quad (1.4)$$

In the MEOS representation, localized (core) charges  $N_{\vec{r}}$  are

$$N_{\vec{r}}^{n+} = -ne^- \hat{D}_{\vec{r}}^n \hat{D}_{\vec{r}}^n, \quad e^- < 0, \quad N_{\vec{R}}^{p-} = pe^- \hat{P}_{\vec{R}} \hat{P}_{\vec{R}}. \quad (1.5)$$

We suppose that both covalent and charge  $2p$ -electrons of an  $O^{2-}$  ion have the wave functions of the same nature. It distinguishes them from  $3d-t_{2g}$  (1.1) and  $4s-3d(e_g)$  (1.3) cation electrons. Here,  $e^-$  stands for electron charge.

The coordinate parts of (1.5) are constant. Their Coulomb interaction reduces to the (constant) Madelung energy [1]. The MEOS spin part (1.3) gives the spin factor

$$N_{\vec{r}\vec{s}} = -ne^- (1 + \vec{S}_{\vec{r}}\vec{S}_{\vec{s}})/(2S+1) \quad (1.6)$$

and results in the Heisenberg model of local spins [1, 2]. The expression of the anion charge operator  $N_{\vec{R}}[\vec{\sigma}_{\vec{R}}]$  is similar. Operators (1.6) are determined in spin spaces of different dimensions. The averaging of the Coulomb energy in these spaces results in the dependence of the Madelung energy on a state of the spin lattice. The spin energy of FM or AFM phases renormalizes the bond energy of a lattice [10].

The MEOS representation allows the direct calculation of exchange energy of the heteropolar (diagonal Coulomb) and homopolar (covalent) nature in Section 2. Local electrical charges (caused by deformation) and their ferroelectric order are considered in Section 3. Their role in CBF spectra and the anomalies of quasiparticles spectra are discussed in Section 4. The phase diagram of ferroelectrics is calculated in Section 5. Comparison with experiment and conclusions are given in Section 6.

## 2. Indirect Exchange inside Sublattices and between Them

The widespread concept of direct exchange [2] is applicable to covalent electrons, which realize interatomic bonds. Only indirect exchange is possible between local spins of ionic cores (or lanthanides' angular moments). In dielectrics, the exchange between local spins  $S_{\vec{r}}$  of magnetic sites  $\vec{r}$  is realised in two ways. The first way - polarization of anions ( $\vec{\sigma}_{\vec{R}}$ ) by overlap of the wave functions of anions and magnetic cations. The second way - through covalent electrons, bonding (or antibonding) of magnetic cations.

Magnetochemical calculations of ferrites are based on a distinction of the  $180$  and  $90^\circ$  configurations of ions [7, 11]. However, the compelled detailed elaboration of 'the trigonometrical model' (expansion of a set of angles) for many-sublattices magnetism loses simplicity and prognostication. One-electronic accounts [12] allow one (at the additional assumptions) to derive some numerical results. However, they do not take into account multielectronic effects (covalency, charge shielding, etc.). It does not allow them to predict the major properties of magnetic phases (magnetization  $M$ ,

the Curie temperature  $T_c$  (or the Neel temperature  $T_N$ ), magnetic anisotropy, etc.). The interpretation of neutron scattering and other data on the distribution of electronic and spin densities [2] will be carried out on the basis of a detailed elaboration of local interionic exchange integrals [2, 7, 11].

The given account has general character. However, for definiteness, we reason by the example of  $3d$ -oxides. The Coulomb (heteropolar)  $d-p$  -bond

$$H^{d-p} = - \sum C(|\vec{l}\vec{l}'|) N_{\vec{r}}^n N_{\vec{R}}^p, \quad \vec{l} \equiv \vec{r} \pm \vec{R},$$

$$C(|\vec{l}\vec{l}'|) > 0 \quad (2.1)$$

in the MEOS representation (1.1) - (1.6) results in the exchange magnetization of an  $O^{2-}$  ion ( $\vec{\sigma}_{\vec{R}}$ )

$$H_{d-p}^{ex} = - \sum A_{d-p} \vec{S}_{\vec{r}} \vec{\sigma}_{\vec{R}},$$

$$A_{d-p} = C(|\vec{l}\vec{l}'|) (\vec{\sigma}_{\vec{R}} \otimes \vec{S}_{\vec{r}}) / 2(2S+1). \quad (2.2)$$

The variational account of  $\vec{\sigma}_{\vec{R}}$  requires the addition of the intraionic (Hubbard) Hamiltonian to (2.2). The cations' covalent bonds are also included [8, 10]:

$$H_{\vec{r}\vec{r}'}^j = \tilde{U}_j N_{\vec{r}}^j N_{\vec{r}'}^j / 2,$$

$$H^{cov} = - \sum_{\vec{r}, \vec{R}} \Gamma_{dd} (|\vec{r} \pm \vec{R}|) \hat{D}_{\vec{r}} \hat{D}_{\vec{R}} -$$

$$- \sum_{\vec{r}, \vec{R}} (\Gamma_{pd} \hat{D}_{\vec{r}} \hat{P}_{\vec{R}} + \text{h.c.}). \quad (2.3)$$

In the MEOS representation, the spin part of Hamiltonian (2.3) is

$$H^s = U_p \sum \vec{\sigma}_{\vec{r}}^2 / 2 - \sum_{\vec{r}, \vec{R}} \hat{\Gamma}^{dd} (\vec{\sigma}_{\vec{r}} \vec{\sigma}_{\vec{R}}) -$$

$$- U_d \sum_{\vec{r}} \vec{s}_{\vec{r}}^2 / 2 - A_i \sum_{\vec{r}} (\vec{S}_{\vec{r}} \vec{s}_{\vec{r}}) -$$

$$- \sum_{\vec{R}, \vec{r}} \hat{\Gamma}^{pd} (\vec{\sigma}_{\vec{R}} \vec{s}_{\vec{r}}). \quad (2.4)$$

The operator coefficients

$$\hat{\Gamma}^{dd} (|\vec{r} \pm \vec{R}|) = f_s \Gamma_{dd} d_{\vec{r}} \bar{d}_{\vec{R}}, \quad \hat{\Gamma}^{pd} =$$

$$= f_s \Gamma_{pd} d_{\vec{r}} \bar{p}_{\vec{R}} \quad (2.5)$$

are used below without spin index (the appropriate generalization is obvious). The further accounts are

accompanied by spur operations in the MEOS spin spaces. The constant  $f_s \leq 1$ .

Spin polarizations of  $O^{2-}$  and covalent electrons are found, varying (2.4) in the variables  $\vec{\sigma}_{\vec{R}}$  and  $\vec{s}_{\vec{r}}$ . It is conveniently to write down the operator equations in the symbolic matrix form as

$$\begin{pmatrix} U_p & -\tilde{\Gamma}^{pd} \\ -\tilde{\Gamma}^{pd} & \hat{U}_d \end{pmatrix} \begin{pmatrix} \vec{\sigma}_{\vec{R}} \\ \vec{s}_{\vec{r}} \end{pmatrix} = \begin{pmatrix} \hat{C}_{dp} (\vec{\sigma} \otimes \vec{S}) \\ A_i \end{pmatrix} \vec{s}_{\vec{r}}, \quad (2.6)$$

where the operator  $\tilde{\Gamma}^{pd}$  is derived from (2.5) by renormalization of the coefficient  $f_s$ . The operators  $\hat{C}$  and  $\hat{U}$ ,

$$\begin{aligned} \hat{C}_{dp} \vec{s}_{\vec{r}} &= \sum_l C(|\vec{l}|) \vec{s}_{\vec{r}+\vec{l}}, \\ \hat{U}_d &= U_d - \sum_{\vec{l}} \hat{\Gamma}^{dd}(|\vec{l}|) \vec{s}_{\vec{r}}^{-1} \vec{s}_{\vec{r}+\vec{l}}, \end{aligned} \quad (2.7)$$

assume the summation on neighbouring cations. The nondiagonal matrix elements (2.6) are essential at the small Hubbard parameters ( $U_p$  or  $U_d$ ).

The general form of solutions is

$$\begin{aligned} \vec{\sigma}_{\vec{R}} &= \Delta^{-1} \{ \hat{C}_{dp} (\vec{\sigma} \otimes \vec{S}) \hat{U}_d + A_i \tilde{\Gamma}^{pd} \} \vec{s}_{\vec{r}} \\ \vec{s}_{\vec{r}} &= \Delta^{-1} \{ A_i U_p + \tilde{\Gamma}^{pd} \hat{C}_{dp} (\vec{\sigma} \otimes \vec{S}) \} \vec{s}_{\vec{r}} \end{aligned} \quad (2.8)$$

The operator determinant of matrix (2.6),

$$\Delta_2 = U_p \hat{U}_d - (\tilde{\Gamma}^{pd})^2, \quad (2.9)$$

should be positive definite. In further estimations, the nondiagonal elements (2.6) are neglected ( $\tilde{\Gamma}^{pd} \rightarrow 0$ ). The restoration of a (bulky enough) general form of the exchange Hamiltonian is obvious.

We substitute (2.8) in (2.1) and (2.4) and derive the spin Hamiltonian (in the Heisenberg form) in the simplified form

$$\begin{aligned} H^{ex} &= \left\{ - \sum_{\vec{r}, \vec{l}} \hat{\Gamma}^{dd}(|\vec{l}|) (A_i / U_d)^2 (\vec{s}_{\vec{r}} \vec{s}_{\vec{r}+\vec{l}}) - \right. \\ &- \sum_{\vec{r}, \vec{l}_1, \vec{l}_2} \hat{C}_{dp}(|\vec{l}_1|) [\hat{C}_{dp}(|\vec{l}_2|) / U_p] \times \\ &\left. \times \sigma^2 S^2 (\vec{s}_{\vec{r}} \vec{s}_{\vec{r}+\vec{l}_1+\vec{l}_2}) \right\} / 2 - O(\tilde{\Gamma}^{pd}). \end{aligned} \quad (2.10)$$

The account of the rejected members ( $\Gamma^{pd}$ ) slightly complicates the interpretation of exchange integrals. A simple form of (2.10) allows us to separate the

exchange contributions (coefficients of the scalar products of spins of the nearest, following, and other neighbours). The diagonal (heteropolar) term has FM sign '+'. The sign of the covalent term depends on the sign of  $\Gamma^{dd}$  (at positivity of the MEOS correlator,  $\langle d_{\vec{r}} d_{\vec{r}} \rangle > 0$ ). Then the bonding cation-cation interaction ( $\Gamma^{dd} > 0$ ) causes the FM exchange bond (at  $A_i > 0$ ). The antibonding (between sublattices) interaction ( $\Gamma^{dd} < 0$ ) defines the AFM exchange integral (sign '-').

The strong (Hubbard) repulsion  $U_p \gg |\hat{C}|$  on an ion  $O^{2-}$  (together with shielding of core charges by covalent electrons) decreases the heteropolar ( $\sim C^2$ ) contribution into (2.10). The covalent contributions in oxides (MeO, Me = Co, Mn, Ni, etc.) depend not only on the Hund parameter ( $A_i$ ), but also on the  $\langle \hat{\Gamma}^{dd} \rangle$  dispersion. The latter defines the strong  $T_N$  dispersion of oxides of 3d-ions ( $100 \leq T_N \leq 500$  K). When the covalent term dominates in (2.10), it is possible to suppose that Ni-Ni bonds are about 10 times stronger than Mn-Mn bonds.

The accounts of orbital polarization are carried out similarly to (2.8). On their basis, the energies of magnetic anisotropy, magnetostriction, etc. are calculated (they will be given in the other place).

### 3. Local Deformations and Electrical Dipoles. Ferroelectricity

The cooperation of electrical dipoles results in the ferro- or antiferroelectrical order. FE ordering of dipoles created above  $T_c$  (on a stabilization of molecules in a crystal) is similar to FM (or AFM) ordering [4, 5]. Application of the mean field theory to them explains many (but far from all) FE properties [5]. The process of creation of local dipoles below  $T_c$  is more interesting. Such FE technically important materials are perovskites (BaTiO<sub>3</sub> and others) [3 - 5]. One of these processes (local deformations) is generally accepted. The model of displacement  $\xi$  of one of ions (Ti [5]) relatively to the oxygen core is used. A change of the configuration of electrical charges  $N_{\vec{r}}(\xi)$  deforms the heteropolar and covalent interactions. The thermodynamic potential (t.d.p.)  $\Phi(0)$  is lowered. The CBF spectra thus are 'softened' and their singular part destabilizes the FE phase (see below in Section 4).

In the method of secondary quantization (in the MEOS representation), it is brought to the expansion of the Hamiltonian coefficients in  $\xi$ . The charges of cations ( $j$ ) or anions ( $p$ ) change at their displacement by  $\vec{l}$  from the equilibrium position in the paraelectric (cubic for perovskites) phase

$$N_{\vec{r}}^{(j,p)}(\vec{l}) = N_{\vec{r}}^{(j,p)}(0) + (\partial N_{\vec{r}}^{(j,p)} / \partial \vec{l}) \vec{l} + \dots \quad (3.1)$$

We suppose further  $|\vec{l}| = l_z = \xi$ . Electrical polarization is [3 - 5]

$$P = q \xi. \quad (3.2)$$

We substitute (3.1) in (2.1). Under the summation sign (integral sign in the continuous approximation on  $\vec{r}$ ), we integrate by parts. The Coulomb (heteropolar) integral is renormalized as

$$C(|\vec{r} - \vec{R}|) \rightarrow C(|\vec{r}_0 - \vec{R}|) + (\partial C / \partial \xi) \xi + \dots \quad (3.3)$$

Similarly, we derive from (2.3) for covalent O<sup>-</sup>Ti(*t*) and Ba<sup>-</sup>O(*b*) bonds

$$\Gamma^{(j,p)}(|\vec{r} - \vec{R}|) = \Gamma^{(j,p)}(|\vec{r}_0 - \vec{R}|) + \gamma_{pj} \xi_j. \quad (3.4)$$

The Fourier expansion of  $\hat{\xi}$  is

$$\hat{\xi}(\vec{r}) = \hat{\xi}_0 + \sum_{\vec{k}} \hat{\xi}_{\vec{k}} e^{i\vec{k}\vec{r}}. \quad (3.5)$$

The Fourier-image (3.5), linear on the phonon Bose operators, enters the Hamiltonian to be multiplied by the MEOS. The CBF singularities "soften" both optical phonons (the soft Cochran modes [3 - 5]), and acoustic phonons. The appropriate account is completely similar to those for FM ferroelastics (see [10]).

#### 4. CBF Spectra in Ferroelectrics

The Fourier expansion for the covalent electron MEOS (1.3) - (1.4) is

$$\begin{aligned} d_{\vec{r}}^j &= d_0^j + \sum_{\vec{k}} d_{\vec{k}}^j e^{i\vec{k}\vec{r}}, \\ d_{\vec{k}}^j &= \sum_{\vec{r}} d_{\vec{r}}^j e^{-i\vec{k}\vec{r}} / N, \quad j = t, b, \end{aligned} \quad (4.1)$$

and

$$\begin{aligned} p_{\vec{r}} &= p_0 + \sum_{\vec{k}} p_{\vec{k}} e^{i\vec{k}\vec{r}}, \\ p_{\vec{k}} &= \sum_{\vec{r}} p_{\vec{r}} e^{-i\vec{k}\vec{r}} / 3N, \quad d_{\vec{r}}^j \bar{p}_{\vec{r}} = K_{jp}. \end{aligned} \quad (4.2)$$

Here, N is the number of cations of each type,  $K_{jp}$  - the operator form of the nonorthogonality integral of wave functions of cation *j* and O<sup>2-</sup>. The designations of the covalent ( $\Gamma^{pj}$ ) and electroelastic ( $\gamma_{pj}$ ) coefficients

are introduced in (3.4). The covalent Hamiltonian is derived as

$$\begin{aligned} H^{\text{cov}} &= -N \sum_j \{ \Gamma^{pj}(0) + \gamma_{pj} \xi_j \} K_{pj} + \\ &+ N \sum_{\vec{k}, j} (\tilde{\Gamma}_{\vec{k}}^{pj} d_{\vec{k}}^j \bar{p}_{\vec{k}} + \text{h.c.}), \end{aligned} \quad (4.3)$$

where

$$\begin{aligned} \tilde{\Gamma}_{\vec{k}}^{pj} &= \Gamma_{\vec{k}}^{pj} - \gamma_{pj} \xi_j, \quad \Gamma_{\vec{k}} = \Gamma(0) - \Gamma(\vec{k}), \\ \Gamma(\vec{k}) &= \sum_{\vec{l}} \Gamma(\vec{l}) e^{i\vec{k}\vec{l}}. \end{aligned} \quad (4.4)$$

Here the CBF interaction with phonons and softening of phonon modes are not taken into account (in particular, ferroelectric defects of elastic moduli  $\hat{C}$ , what will be made in the other place). Their account overloads the account of thermal properties, in particular, the dependence of polarization  $P(T)$  on temperature  $T$ .

The cation covalent bond also is not taken into account (as an effect of the following order of smallness in perovskites). We would recall (see Section 2) that the latter is important for account of exchange integrals, for example, on the coexistence of AFM and ferroelectric orders [4]. The anticommutator (two-time Bogolyubov') Green functions for MEOS [8, 10] are introduced as

$$G_{\vec{k}}^{j(p)} = \langle \langle \bar{d}_{\vec{k}}^j(\bar{p}_{\vec{k}}) | d_{\vec{k}}^t \rangle \rangle. \quad (4.5)$$

The motion equations for them are deduced as follows:

$$\begin{pmatrix} E & \tilde{\Gamma}_{\vec{k}}^{bp} & 0 \\ \tilde{\Gamma}_{\vec{k}}^{bp} & E & \tilde{\Gamma}_{\vec{k}}^{tp} \\ 0 & \tilde{\Gamma}_{\vec{k}}^{tp} & E \end{pmatrix} \begin{pmatrix} G_{\vec{k}}^b \\ G_{\vec{k}}^p \\ G_{\vec{k}}^t \end{pmatrix} = 1/N \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}. \quad (4.6)$$

The secular equation (determinant of (4.6)),

$$E^3 - E \sum_j |\tilde{\Gamma}_{\vec{k}}^{pj}|^2 = 0, \quad (4.7)$$

has a nonphysical solution ( $E = 0$ ). The latter becomes nontrivial after the account of covalent bonds between cations. Its contribution into t.d.p. is of the following order of smallness and is not taken into account here.

Two branches of the solutions for CBF,

$$E_{\vec{k}}^{\pm} = \pm \left\{ \sum_j [|\Gamma_{\vec{k}}^{pj}|^2 - 2 \text{Re}(\Gamma_{\vec{k}}^{pj} \gamma_{pj} \xi_j)] + \right.$$

$$+ (\gamma_{pj} \xi_j^2)^2 \}^{1/2}, \quad (4.8)$$

are nonmonotonous functions of  $k$  in the FE phase. Their singularities destabilize the FE phase and are responsible for anomalies of physical (FE and other) properties. Further simplification is in use of the model [5] for bonding ( $\Gamma^{pt} > 0$ ) interactions

$$\gamma_{pj} = \gamma \delta_{jt}, \quad \xi_j = \xi \delta_{jt}, \quad \text{when } \gamma > 0, \quad \Gamma \frac{p_j}{k} = \Gamma_j \vec{k}^2. \quad (4.9)$$

(The generalization of the theory on the basis of (4.8) introduces additional parameters, which are easily taken into account. It diversifies the FE phase diagram. The latter is essential for BaTiO<sub>3</sub>). The CBF spectra of paraelectric phase,

$$E_k^{\pm}(\xi = 0) = \pm \Gamma_c \vec{k}^2, \quad \Gamma_c = \left( \sum_j \Gamma_j^2 \right)^{1/2},$$

$$\Delta \Phi^{\text{CBF}} = \alpha_c \tau_c^{5/2}, \quad \tau_c = k_B T / \Gamma_c, \quad (4.10)$$

have simple (parabolic) form. Here,  $k_B$  is the Boltzmann constant.

The CBF spectra of the ordered FE phase have extrema. Their singularities change the CBF contribution to t.d.p.  $\Delta \Phi_t(T)$ . The singular part of CBF is approximated by lines

$$E_k^{\pm}(\xi) \approx (E_0 - gk), \quad k \leq Q = E_0/g, \quad E_0 = \gamma \xi > 0. \quad (4.11)$$

It should be noted that the choice of the signs of  $\xi$  and  $\gamma$  is many-valued. It is necessary only to keep  $(\gamma \xi) > 0$ . Contribution (4.11) to t.d.p. (for the Fermi distribution function with chemical potential equal to zero)

$$\Delta \Phi_t^{\text{CBF}} \approx v_1 g \times$$

$$\begin{cases} [(Q/\beta g)^{-2} + \sum_{n=2}^{\infty} C_{n1} Q^2 (\beta g n)^{-2}], & \text{when } \beta g \gg 1, \\ [A - v_2 Q^5 (\beta g) + \\ + \sum_{n=2}^{\infty} C_{n2} Q^5 (\beta g)^{2n-1}], & \text{when } \beta g \ll 1, \beta = 1/k_B T \end{cases} \quad (4.12)$$

depends differently on  $T$  near  $T_c$  for low  $T_c$  (as BaTiO<sub>3</sub>) or high  $T_c$  (as LiNbO<sub>3</sub>,  $T_c = 1470$  K [1]). The dependence  $Q(\xi)$  is defined, besides other, by the ratio  $(\gamma/\Gamma_c)$ .

Singularities (4.11) deform the quasiparticles spectra (at their crossing with CBF branches). The large values of  $|\gamma|$  provide a strong phonon-electronic bond. When CBF cross different phonon branches, the anomaly ("softening") of the latter should be very significant. This conclusion proves to be true by experiments near  $T_c$  [1, 3 - 5]. More detailed experiments in the FE phase are desirable.

## 5. Ferroelectric Phase Diagram

The t.d.p. dependence on deformation  $\xi$  is calculated on the basis of (3.3) and (4.12). The t.d.p. term linear in  $\xi$  can have different signs. It depends on the values and signs of hetero- and homopolar terms (3.3) and (3.4). The term, which has the square-law dependence on  $\xi$ , is also composed from the energies of different natures. However, its physical sense is obvious. It is the elastic modulus  $C_e$  (or rather the combination of elastic moduli in the general case of low-symmetric deformations tensor  $\xi$ ). The difference of t.d.p. of the FE ( $\xi \neq 0$ ) and paraelectric ( $\xi = 0$ ) phases,

$$\Delta \Phi(\xi) = C_e \xi^2/2 - \gamma_t \xi - \alpha_c \tau_c^{5/2} +$$

$$+ g_2 T^2 L(\xi), \quad \beta g \gg 1, \quad (5.1)$$

gives sharply differing dependences  $\xi(T)$ . It is functionally caused by a form of  $L(\xi)$ . Here,  $\gamma_t$  is the combination of the inhomogeneity parameters  $\gamma_{jp}$  and others and the nonorthogonality integrals  $\langle K_{pj} \rangle$  (4.2). The similar combinations are contained in the function  $L(\xi)$ .

The polynomial form is assumed:

$$L(\xi) = 1 + \sum_{m=1}^{\infty} b_m \xi^m / m!, \quad b_m \ll 1. \quad (5.2)$$

We take  $m = 1$ . By varying (5.1) on  $\xi$ , we get

$$\xi = \xi_0 - \xi_2 T^2, \quad \xi_0 = \gamma_t / C_e, \quad \xi_2 = \xi_0 g_2 b_1 / C_e, \quad b_1 > 0. \quad (5.3)$$

The sign of  $\xi$  (stretching or compression) is defined by  $\gamma_t$ . We substitute (5.3) in (3.2) and obtain

$$P(T) = P(0) - P_2 T^2. \quad (5.4)$$

The temperature of the first kind transition  $T_c$  is found from Eq. (5.1) as

$$\Delta\Phi(\xi, T_c) = 0, T_c \approx |\gamma_t| / (2C_e g_2)^{1/2},$$

$$\xi(T_c) = \xi_0 (1 - b_1 \xi_0^2), \quad (5.5)$$

neglecting ( $\Gamma_c \rightarrow \infty$ ) the CBF contribution of the para-phase and the sum in (5.2). The jump of spontaneous polarization  $P(T_c)$  at the transition point is close to  $P(0)$ . It is coordinated with data on perovskites.

The alternate variant  $b_1 \gg 1$  results in the second kind transition

$$P = q \xi_0 (1 - T^2/T_c^2), T_c = (\gamma_t/g_2 b_1)^{1/2}, \quad (5.6)$$

that is coordinated with data on triglycinesulphate (TGS) [1]. A more complex  $P(T)$  for  $\text{KH}_2\text{PO}_4$  or the Seignette salt (two Curie points at  $\pm 20^\circ\text{C}$ ) requires the detailed account of the CBF branches. In many-atomic crystals, there are more CBF branches and t.d.p.  $\Phi(\xi, T)$  has complex enough (multiparametric) form.

**6. Comparison with Experiment and Conclusions**

The variety of bonding and antibonding covalent interactions, as well as the attracting and repulsing Coulomb (ionic) interactions, favours exchange integrals of different signs. In many-atomic dielectrics, it results in the formation of a diversity of many-sublattice FM and AFM structures. The experiment [1, 2, 7, 13] confirms the dependence of the magnetic order on local atomic bonds. The latter define the values and signs of local exchange energies of different sublattices.

The reception of new, complex enough, ferroelectric (attractive, for example, for electronics [14]) requires a detailed consideration of ion interactions [15]. It is possible on the basis of the multielectronic quantum theory with the obligatory account of thermal fluctuations of the interionic interactions (CBF). Such a theory is proposed in the given work.

Specific conclusions:

1. Exchange interactions of a dielectric spin lattice are formed: 1) by the heteropolar bonds at anion spin polarization, 2) by the covalent bonds of magnetic cations at the Hund magnetization of bonding (FM exchange) or antibonding (AFM exchange) electrons.

2. Antibonding covalent interactions favour the division into AFM sublattices. The competition of the exchange energies of hetero- and homopolar natures

defines the Neel temperatures  $T_N$  and paramagnetic temperatures  $\Theta$ .

3. Deformations  $\xi$  create local dipole moments and change the bond energies. Nonhomogeneities of electric charges  $N_T(\xi)$  and covalent bond energies  $\Gamma(\xi)$  result in the dependence of the Hamiltonian in the MEOS representation on  $\xi$ . Ferroelectric polarization  $P \sim \xi$ .

4. Singularities of CBF spectra of the ferroelectric phase deform ('soften') the spectra of other quasiparticles (phonons, etc.).

5. The contribution of CBF singularities to t.d.p.  $\Delta\Phi_t(\xi, T)$  strongly depends on  $T$ . It destabilizes the ferroelectric phase.

6. The type of functional dependence  $\Delta\Phi(\xi)$  defines the ferroelectric transition kind. The ratio  $(\Gamma/\gamma)$  plays a role, where  $\gamma$  is the nonhomogeneity energy. The deformation  $\xi \sim \gamma$ .

7. The large value  $\xi$  (and polarization  $P$ ) defines the first kind transition (in perovskites like  $\text{BaTiO}_3$ ). The polarization jump  $P(T_c) \approx P(0)$ .

8. The small value  $\xi$  favours the second kind transition (in TGS and the Seignette salt). The calculated function  $P(T) \sim 1 - (T/T_c)^2$  is coordinated with experiment [5].

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