Ferroelectric phase transitions in cubic perovskites

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Abstract. In low-temperature phase, due to the pseudo Jahn-Teller effect in unit cells, atoms are coherently localized in one of eight trigonal wells of the adiabatic potential energy surface. With temperature, nuclear motion delocalizes over symmetry-equivalent wells. Depending on the size of potential barriers, the two limiting cases are considered: (a) shallow wells, and (b) deep wells. They correspond to two different mechanisms of delocalization. When potential barriers are shallow compared to $kT_C$, the delocalization is due to over-the-barrier activation of Arrhenius type. Alternatively, when the over-the-barrier activation is thermally inaccessible, the delocalization is due to tunnelling. Temperature dependence of spontaneous polarization is treated in terms of the mean-field approximation. Using experimental data for BaTiO$_3$, numerical values of the corresponding parameters are estimated. The qualitative description is followed by a numeric evaluation of the temperature sequence of ferroelectric phase transitions for the two cases of shallow and deep wells. The theory agrees with the experimental data.

1. Introduction

Discovered in 1920, ferroelectricity is over ninety years old already. Yet some fundamental questions about its microscopic nature remain unanswered. Here, in this brief introduction, we cannot give a comprehensive review of this vast trend in physics of solid state. The references listed below are to just provide a general perspective of some ideas and basic concepts in the modern theory of ferroelectricity. More elaborate introduction to the problem is given by Bersuker [1].

The traditional understanding of ferroelectricity is based on the phenomenological approach of Ginsburg [2], Devonshire [3], Cochran [4], Anderson [5], and Landau [6]. It explains ferroelectric phase transitions as resulting from competition of the short-range inter-ionic repulsion with the long-range dipole-dipole attraction via the limiting-phonon TO mode. This led to the concept of soft mode that goes to zero at the point of a phase transition. It was experimentally observed in many ferroelectric crystals.

In its present form, the phenomenological theory can be found in different texts on solid-state physics and, also, in specialized monographs and review papers on ferroelectricity, particularly, in Lines and Glass [7], Rabe et al. [8], Smolenskii [9], and Dawber et al. [10]. The phenomenological theory was not intended to and does not provide any systematic way to deduce how chemical composition of a particular crystal determines its ferroelectric properties.

The early attempts to answer this question went in two different directions. One is the so-called electronic theory. Launched by Wigner [11] and Jaynes [12, 13], it relates the bulk polarization of a ferroelectric crystal solely to the electron polarizability of the composition ions. The polarizability implies electron hybridization of the ground-state electron wave function with some excited (unoccupied) opposite-parity electron states. Providing flexibility to the ground-state wave function, electron hybridization allows it induce a local dipole moment.
For cubic perovskites $ABO_3$, the band gap to the polar states is of the order of 3 eV. With this gap, the ionic polarization is an order of magnitude less than the one experimentally observed. From another hand, to obtain the measured value of polarization, one has to assume an energy gap as small as 0.13 eV [10] which is 20 times smaller than the observed gap. Due to this inconsistency the electronic theory was rejected.

The other way was assuming a significant anharmonicity of the crystal lattice. The overall polarization of the crystal was presumed to be purely due to displacements of crystal-lattice atoms into low-symmetry off-centre minimum positions on the adiabatic potential energy surface (APES). In a central-symmetrical crystal structure, polar displacements of charged ions create local dipole moments. Originating from Mason and Matthias [14] this idea was developed by Devonshire [3, 15] and Slater [16]. Atomic displacements were measured quite accurately in X-ray diffraction experiments. To explain the observed polarization, unusual electric charges were assumed (the so-called Born charges) of the displaced atoms. For example, in BaTiO$_3$, the Born charge of Ti was found to be close to +7 [8-10]. Evidently, sharing and donating its four valence electrons, Ti cannot have an electric charge greater than +4.

It is important to note that both approaches turned out to be quantitatively inconsistent and failed when applied to cubic perovskites. The corresponding discussion of their deficiency can be found elsewhere [7 - 10]. Also, today there are quite a number of papers that combine both approaches. They start with a model Hamiltonian with its parameters taken from a first-principles electronic structure calculation of the lowest APES; e.g. see [17, 18] and references therein.

**Figure 1.** The octahedral fragment of the cubic perovskite crystal structure $ABO_3$, with the transition metal atom $B$ at the centre (solid red) and six oxygen atoms (blue) at the apexes of the octahedron. The characters $a$, $b$, $c$, etc. denote the eight off-centre positions (not to scale) of the atom $B$ induced by the pseudo JTE. The counter-phase displacement of the oxygen atoms is not shown.

In this paper we follow the vibronic approach first introduced by Bersuker in 1966 [19]. Its more elaborate version was published in 1967 [20]. The basic idea is local instability of octahedral fragments [BO$_6$] in a cubic perovskite $ABO_3$ (Fig.1) due to the pseudo Jahn-Teller effect (JTE). The physical nature of the pseudo JTE is the electron-vibrational (vibronic) hybridization of valence (occupied) electron orbitals with some excited (unoccupied) electron states involved in this coupling. The general idea of the pseudo JTE was introduced in 1957 by Öpik and Pryce [21] for the simple example of linear triatomic molecules, $ABA$. Somewhat different version of the vibronic approach in terms of electron and phonon bands (sometimes called “the two-band theory” or “the interband model”) was introduced by Kristoffel and Konsin in 1967 [22].

A general review of the pseudo JTE can be found in the books [23, 24]. The vibronic coupling is known to result in a significant anharmonicity of the lowest APES. The high-symmetry point can be a
minimum or a maximum depending on the relative value of the Jahn-Teller stabilization energy, $E_{JT}$, and the energy gap, $\Delta$, separating the valence (occupied) electron shell from the excited (unoccupied) orbitals involved in the vibronic coupling (Sect. 2).

In cubic perovskites, the vibronic coupling involves three polar modes, $X$, $Y$, and $Z$, of a unit cell. They correspond to an off-center displacement of the cation $B$ and a counter-direction displacement of the oxygen octahedron. In barium titanate, the band gap is of the order of 3 eV. For the Jahn-Teller stabilization energy, $E_{JT}$, a rough estimate gives $E_{JT} \approx 4$ eV, greater than the energy gap (Sect. 2); so the vibronic coupling is strong enough and the criterion of the pseudo Jahn-Teller instability holds.

This paper is organized in the following way. In Section 2, we start with the ground-state APES for the octahedral fragment $[BO_6]$ in a perovskite structure $ABO_3$ (Fig. 1) in the form that results from the vibronic hybridization (the pseudo JTE) of the highest-occupied molecular orbitals (HOMO) with the lowest unoccupied molecular orbitals (LUMO). Particular attention is paid to the case of barium titanate. The corresponding parameters of the theory are estimated from measured data. In Section 3.1, the mean-field approximation is introduced. It reduces the issue of structural instability of the ferroelectric crystal to the problem of instability of one unit cell in the average field of all other unit cells of the crystal. In Section 3.2, this problem is solved in a self-consistent way and the corresponding phase diagrams are discussed. We will consider the two limiting cases: (a) shallow wells, and (b) deep wells. As will be shown, they correspond to two different mechanisms of delocalization. When potential barriers are shallow compared to $kT_C$, the delocalization is due to over-the-barrier activation of Arrhenius type. Alternatively, when the over-the-barrier activation is thermally inaccessible, the delocalization is due to tunneling of the system between symmetry-equivalent potential wells. The respective phase transitions are treated as order-disorder ones. In Section 4 we discuss different pro- and contra- arguments for the order-disorder character of ferroelectric phase transitions in cubic perovskites. From entropy arguments it follows that the actual crystal structures include ordered clusters of a finite size. From this point of view, discussed in this paper order-disorder phase transition should be understood as a rather simplified description of the real-life case.

2. Zero temperature: the ground-state APES in barium titanate

Following Bersuker [1], consider the octahedral fragment of the unit cell centered at the transition metal atom $B$ (solid red circle in Fig. 1). It is surrounded by six oxygen atoms (blue circles in Fig. 1). In the MO LCAO presentation, the HOMO are formed by nine $2p_z$ orbitals of the six oxygen atoms. They transform as the irreducible representations $t_{1u}$, $t_{2u}$, and $t_{1g}$ of the octahedral symmetry group. The LUMO are $t_{2g}(3d)$ orbitals of the transition metal $B$, namely, $|yz(B)\rangle$, $|xz(B)\rangle$, and $|xy(B)\rangle$. As one can see in Fig. 2, in the high-symmetry configuration, when the atom $B$ is in the center of oxygen octahedron, the HOMO-LUMO overlap is zero. Therefore, when the transition atom $B$ is at the center of the oxygen octahedron, these orbitals are non-bonding; they do not contribute to the chemical bonding of the transition metal with the oxygen atoms.

**Figure 2** Zero overlap (shaded) of the oxygen HOMO with the metal LUMO in the high-symmetry cubic configuration. Shown is the particular case of the oxygen symmetry-adapted orbital $|T_{1u}\rangle$ and the $|T_{2g}\rangle$ orbital of Ti$^{4+}$. An off-centre displacement of Ti$^{4+}$ creates a non-zero overlap resulting in an additional covalent chemical bond of oxygen atoms with Ti$^{4+}$ [1, 25].
An off-center displacement of the central ion, \( Q = \langle X, Y, Z \rangle \), changes the HOMO-LUMO overlap to a non-zero value forming an additional covalent bond [19, 20 24-27]. Correspondingly, with the additional bond, the total energy of the unit cell lowers. This energy benefit is the origin and physical nature of the pseudo JTE in cubic perovskites. If strong enough, it may trigger the dipole instability in every unit cell resulting in ferroelectric phase transitions.

For the octahedral fragment \([BO_6]\), the one-electron Hamiltonian can be expanded in a power series with respect to \( Q \). With up to linear terms included, we come to the Jahn-Teller Hamiltonian, \( H_{JT} = \Delta \hat{A} + F_0 Q \cdot \hat{d} \). It includes the zero-order term of the expansion (the energy gap term), \( \Delta \hat{A} \), and the linear term of the Jahn-Teller coupling, \( F_0 Q \cdot \hat{d} \). Here \( \hat{A} \) is the diagonal matrix \( 9 \times 9 \) acting within the manifold of the nine electron orbitals, namely, the six HOMO and the three LUMO, so the energy gap between HOMO and LUMO is \( 2\Delta \). \( F_0 \) is the constant of linear pseudo Jahn-Teller coupling, the so-called orbital vibronic coupling constant,

\[
F_0 = \left\{ 2p_z(0) \left[ \frac{\partial H}{\partial Q} \right]_0 \right\}^{3d_{\alpha}}(Ti).
\]

Also, we introduced three matrices \( 9 \times 9 \), \( \hat{d} = \{ \hat{d}_x, \hat{d}_y, \hat{d}_z \} \) of the electric dipole moment of electrons, \( d \). Its reduced matrix element is incorporated in \( F_0 \).

The Jahn-Teller Hamiltonian, \( H_{JT} \), is a matrix \( 9 \times 9 \) acting in the basis set of the six HOMO and the three LUMO. Its nine eigenvalues correspond to one-electron energy levels that change adiabatically with respect to the off-center position of the transition-metal \( B \). In the case of barium titanate, the octahedron is \([TiO_6]\) and there are twelve valence electrons populating the hybridized HOMO. Benefiting in energy from the new covalency created by the polar distortions, \( Q_x, Q_y, \) and \( Q_z \), these twelve electrons contribute to the following potential energy of the lowest APES [1, 19, 21, 24-26],

\[
U(Q) = \frac{1}{2}K_0Q^2 - 2\left[ \sqrt{\Delta^2 + 2F_0^2\left(Q^2 - X^2\right)} + \sqrt{\Delta^2 + 2F_0^2\left(Q^2 - Y^2\right)} + \sqrt{\Delta^2 + 2F_0^2\left(Q^2 - Z^2\right)} \right].
\]

Here, in addition to the eigenvalues of the Jahn-Teller Hamiltonian, \( H_{JT} \), we introduced the elastic energy, \( \frac{\gamma K_0(X^2 + Y^2 + Z^2)}{\gamma K_0} = \frac{\gamma K_0}{\gamma} \), associated with the off-center displacement of the central ion. \( K_0 \) is the respective primary force constant. Expressed by \( K_0 \), the corresponding elasticity is due to \( \sigma \) orbitals and ionic interactions. The expression (2) for the ground-state APES follows from first principles applied to the pseudo JTE in cubic perovskites. Its elaborate explanation, detailed derivation, and analysis was given by Bersuker [19, 20, 24-27]; also, see [1].

Introducing dimensionless parameters \( u, \delta, x, y, \) and \( z \) such that

\[
U = u \frac{F_0^2}{K_0}, \quad \Delta = \delta \frac{F_0^2}{K_0}, \quad X = x \frac{F_0}{K_0}, \quad Y = y \frac{F_0}{K_0}, \quad Z = z \frac{F_0}{K_0},
\]

the ground-state APES can be presented in the dimensionless form,

\[
u(x, y, z) = \frac{1}{2}\left[ \sqrt{\delta^2 + 2\left(r^2 - x^2\right)} + \sqrt{\delta^2 + 2\left(r^2 - y^2\right)} + \sqrt{\delta^2 + 2\left(r^2 - z^2\right)} \right],
\]

with \( r^2 = x^2 + y^2 + z^2 \).

In a close vicinity of the high-symmetry point, \( x = y = z = 0 \), the ground-state APES is a spherical paraboloid,

\[
u \approx \frac{1}{2\delta}(\delta - 8)r^2 - 6\delta.
\]

The respective (dimensionless) curvature is \( 1 - 8/\delta < 0 \) and is open up in the opposite case. Correspondingly, on the ground-state APES expressed by the Eq.1, the high-symmetry point, \( X = Y = Z = 0 \), is a maximum when \( 0 < \delta < 8 \) (equivalently, \( \Delta < \)).
8(F0)2/K0) and is a minimum in the opposite case, when δ > 8 (equivalently, when Δ > 8(F0)2/K0). In the former event, the octahedron [TiO3] is unstable with respect to the polar distortions, X, Y, and Z. As mentioned above, this instability is due to the pseudo JTE [1, 19]. The inequality 0 ≤ δ ≤ 8 [or, equivalently, Δ < 8(F0)2/K0] is the condition of instability in this particular case. There is a rigorous proof [27] that the pseudo JTE is the only possible source of this kind of instability in cubic perovskites.

In the case of a relatively strong vibronic coupling, when δ < 8, in addition to the high-symmetry maximum at x = y = z = 0, the potential surface (4) has three kinds of extreme points. For the dimensionless APES expressed by Eq.4, the equipotential cross-sections are mapped onto the surface of the unit sphere shown in Fig. 3. There are eight trigonal wells at (±r0, ±r0, ±r0) with r0 = ½(64 − δ2)1/2. The corresponding stabilization energy, u(0, 0, 0) - u(r0, r0, r0), is EJT(111) = ⅛(8 − δ). The trigonal wells are separated by twelve orthorhombic potential barriers at (±r1, ±r1, 0), (±r1, 0, ±r1), and (0, ±r1, ±r1) with r1 ≈ 0.6(64 − δ2)1/2. The stabilization energy, u(0, 0, 0) - u(r1, r1, 0), is

EJT(110) ≈ 0.35(8 − δ)2. The height of the orthorhombic potential barriers is Δu = EJT(110) - EJT(111) ≈ 0.028(8 − δ)3. Finally, there are six tetragonal saddle points at (±r2, 0, 0), (0, ±r2, 0), (0, 0, ±r2) with r1 = r0√2 = ½[2(64 − δ2)]1/2. The corresponding stabilization energy is u(0, 0, 0) - u(r2, 0, 0) = EJT(100) = ¼(8 − δ)2.

The curvature of the APES at the trigonal minimum points is obtained from the eigenvalue problem for the matrix of second derivatives of u(x, y, z) in (4). At each trigonal well, the three normal frequencies split into a non-degenerate and a two-fold degenerate one. The non-degenerate mode corresponds to a longitudinal vibration along [111]. The two-fold degenerate E mode corresponds to transverse vibrations perpendicular to the direction [111]. The respective curvatures are KA = 1 − (δ/8)2 and KE = ¼KA.

2.1. Estimating parameters of the APES for barium titanate.
For BaTiO3, available experimental data and, also, the results of ab initio calculations allow us to estimate the parameters of the APES. Of the three independent parameters that determine the polar
instability, $\Delta$, $F$, and $K_0$, the energy gap, $\Delta$, is relatively well known, $2\Delta \approx 3.25$ eV. The remaining two parameters can be obtained from the experimental value of the off-centre displacement of the ion Ti$^{4+}$ in the trigonal well, $Q_0 \approx 0.11$ Å, and from the Jahn-Teller stabilization energy, $E_{JT}(111)$, in the trigonal well. From XAFS, this energy is about 0.2 eV [28] while from ab initio calculations, $E_{JT}(111) \approx 0.3$ eV [29], slightly different but of the same order of magnitude. The difference is quite understandable. The latter value is calculated for the rhombohedral phase where the distortion is enhanced by the mean field of the crystal, whereas the XAFS experiments are performed in the paraelectric phase, and hence reflect just the local distortion. For our local model the former value, $E_{JT}(111) \approx 0.2$ eV, is more appropriate.

Another option to involve experimental data is to exploit vibrational frequencies. In particular, in the trigonal well, the transversal vibration, $\hbar \omega_E$ (the one perpendicular to the axis [111]), may be assumed to approximately represent the soft mode at low temperatures. The usual estimate is $\hbar \omega_E \approx 100$ cm$^{-1}$ [30]. The vibrational frequencies and, respectively, the vibrational quanta, $\hbar \omega_0$, $\hbar \omega_A$, and $\hbar \omega_E$, depend on the reduced mass, $M = \frac{m_1 m_2}{m_1 + m_2}$, where $m_1$ is mass of the transition-metal atom and $m_2$ is cumulative mass of oxygen atoms participating in the polar displacements. In cubic perovskites, $ABO_3$, there are three oxygen atoms per each atom $B$. Then $m_2 = 3(16 \text{ u}) = 48$ u. In the case of barium titanate, $m_1 = 48$ u and, therefore, $M = 24$ u. The two versions of the numerical estimate of all the relevant parameters are given in the Table 1.

As one can see, in spite of essentially different experimental data used in the two estimates, the numeric values are quite reasonable and rather consistent (within the expected orders of magnitude). Although the electron energy gap, $2\Delta \approx 3.25$ eV, is relatively large, the pseudo JTE is even stronger providing the polar instability in both versions of the Table 1. The corresponding stabilization energy, $16F^2/K_0$, equal to 3.98 eV and 3.75 eV in the versions I and II respectively, is greater than the gap, $2\Delta = 3.25$ eV. On the other hand, the condition of instability may be very restricting, which is why it is not the case in other similar systems.

Table 1. Numerical values of the parameters of the pseudo JTE, introduced in Eqs.2 and 3, obtained from the comparison of experimental data with the calculated APES. Two versions based on the two sets of data are given.

| Main parameters | Version I $[E_{JT}(111) = 0.2$ eV$]$ | Version II $(\hbar \omega_E = 100$ cm$^{-1})$ |
|-----------------|-------------------------------------|-----------------------------------------------|
| $K_0$ | 13.3 eV/Å$^2$ | 11.0 eV/Å$^2$ |
| $\hbar \omega_0$ | 388 cm$^{-1}$ | 354 cm$^{-1}$ |
| $F_0$ | 1.82 eV/Å | 1.65 eV/Å |
| $(F_0)^2/K_0$ | 0.249 eV | 0.246 eV |
| $F_0/K_0$ | 0.137 Å | 0.149 Å |
| $\delta$ | 6.54 | 6.60 |
| $E_{JT}(111)$ | 0.20 eV | 0.181 eV |
| $Q_0 = (F/K_0)\rho_0$ | 0.11 Å | 0.11 Å |
| $\hbar \omega_A$ | 224 cm$^{-1}$ | 200 cm$^{-1}$ |
| $\hbar \omega_E$ | 112 cm$^{-1}$ | 100 cm$^{-1}$ |
| $E_{JT}(110)$ | 0.1867 eV | 0.169 eV |
| $\Delta E_{JT} = E_{JT}(111) - E_{JT}(110)$ | 108 cm$^{-1}$ | 98 cm$^{-1}$ |

In the ground-state APES (1) and its dimensionless equivalent (4), the significant anharmonicity is obtained without involving the anharmonic terms in the Hamiltonian; only the linear vibronic coupling is included. On the other hand, without the pseudo JTE included in the Hamiltonian, just the singlet anharmonicity with even up to the forth-order terms does not create the eight-minimum APES [15]. Thus, with its eight trigonal wells, twelve orthorhombic saddle points, and six tetragonal saddle points, the APES (1) is a sole result of the pseudo JTE [1,19,20]. By the vibronic hybridization of the ground
and excited electronic states, it generates the so-called “vibronic anharmonicity” [24] which is much more ample than the singlet anharmonicity introduced directly in the Hamiltonian.

3. Rising the temperature. The mean-field approximation.
In ferroelectrics the temperature dependence of spontaneous polarization is due to the special anharmonic shape of the APES (Section 2). On the APES of cubic perovskites, the only kind of minimum points are the trigonal wells. Therefore, at low temperatures, in each unit cell the vibrational motion of atoms is localized at the bottom of a trigonal well. It corresponds to an off-center displacement of the transition metal ion along one of the eight equivalent trigonal directions. The inter-cell interaction is minimized when the off-center displacements in different unit cells and the corresponding dipole moments are ordered forming a low-symmetry phase.

When the local dipole moments are ordered, they determine the overall polarization of the crystal as a whole. Respectively, the spontaneous polarization of the unit cells induces a non-zero electric field, the mean field of all unit cells. Depending on the character and sign of the inter-cell coupling, the ordered phase can be ferroelectric, antiferroelectric, or of a more complex kind. For barium titanate, the vibronic approach predicts the low-temperature ferroelectric phase with all Ti atoms in a correlated off-center position along the same trigonal direction [1, 19, 20].

The mean field and the ordered off-center position of the Ti atoms are interdependent in a self-consistent way. With temperature, Boltzmann population of excited energy levels grows. When the temperature excitation in trigonal wells approaches the height of next-in-energy orthorhombic potential barriers, the system averages out over two nearest-neighbor trigonal wells along, say, \([111]\) and \([11\bar{1}]\), by hoping or tunneling over the orthorhombic barrier. The crystal becomes disordered along one of its symmetry axes, the \(z\) axis in this example, remaining ordered along the other two. At average, the crystal is polarized along \([110]\). Macroscopically, this type of ordering is equivalent to the orthorhombic phase. Correspondingly, the orientation of the mean field changes to \([110]\). Still, lowered by the mean field, this pair of potential wells is separated from the other equivalent ones by tetragonal potential barriers that are higher in energy.

By a farther increase in temperature, higher-energy states become temperature populated, their energy reaching the higher potential barrier with the tetragonal saddle point, say, \([100]\) on its top. The crystal structure transforms into the tetragonal phase with four directions of disorder. The average polarization and the induced electric field change to the one along \([100]\). This is the so-called tetragonal phase (Table 2). Finally, when the temperature is high enough, the maximum of the adiabatic potential at \(X = Y = Z = 0\) is overcome. The local dipole moments become averaged over all eight trigonal wells, and the crystal reaches the completely disordered paraelectric phase. Worth to mention, deduced from the vibronic approach, this qualitative description of ferroelectric phase transitions in BaTiO\(_3\) was first predicted in 1966 [19]. Today it is a common knowledge supported by multiple experiments [7].

3.1. The mean-field theory.
To quantify this qualitative description, consider the Hamiltonian of a cubic perovskite crystal \(ABO_3\) as the following sum over different unit cells:

\[
H = \sum_{m} H_{m} + \sum_{m \neq n} H_{mn}.
\]

Unit cells are labeled with vector indexes \(m = (m_x, m_y, m_z)\) and \(n = (n_x, n_y, n_z)\). The one-cell Hamiltonian, \(H_m = H_0(m) + H_{JT}(m)\) is the same as the one introduced above in Section 2 with the only difference, this time it has the index \(m\) of the unit cell.

The off-center displacement of the atom \(B\) creates a nuclear dipole moment which, in its turn, induces a local dipole moment of valence electrons. The respective mechanism involves a non-zero HOMO-LUMO overlap discussed in Section 2 (Fig.2). Employing the operator of the electric dipole
moment, \( d_m \), of electrons associated with \( m \)-th unit cell, the Hamiltonian of inter-cell coupling can be presented as follows:

\[
H_{mn} = \frac{1}{2} f_{mn} \hat{d}_m \cdot \hat{d}_n + F_{mn} Q_m \cdot \hat{d}_n + \frac{1}{2} K_{mn} Q_m \cdot Q_n. \tag{7}
\]

The reduced matrix element of the operator \( \hat{d}_m \) is incorporated in the coupling parameters \( f_{mn} \) and \( F_{mn} \).

They decrease with the inter-cell distance as \( |m-n|^{-3} \).

The inter-cell coupling (7) can be derived directly from the first principles. In what follows, the coupling parameters, \( f_{mn} \) and \( F_{mn} \), will combine into the inter-cell correlation constant. It will be determined from fitting to experimental data. Therefore, the direct relation of the Hamiltonian (7) to the first-principle parameters of the theory is unnecessary here.

To decouple the Hamiltonian (7), we apply the mean-field approximation. It is introduced in the traditional way, similar to how it is done in the theory of magnetic phase transitions. In a ferroelectric phase, the temperature averages \( \langle \hat{d}_m \rangle \) and \( \langle Q_m \rangle \) do not depend on the cell index \( m \). This means we can assume \( \langle \hat{d}_m \rangle = \langle d \rangle \) and \( \langle Q_m \rangle = \langle Q \rangle \). Also, compared to the average values, \( \langle d \rangle \) and \( \langle Q \rangle \), the fluctuations, \( \Delta \hat{d}_m = \hat{d}_m - \langle d \rangle \) and \( \Delta Q_m = Q_m - \langle Q \rangle \), are assumed to be small. Plugging \( \hat{d}_m = \langle d \rangle + \Delta \hat{d}_m \) and \( Q_m = \langle Q \rangle + \Delta Q_m \) into the Hamiltonian (7), it is transformed into a quadratic form of the fluctuations \( \Delta \hat{d}_m \) and \( \Delta Q_m \). As the fluctuations are assumed to be small, the terms quadratic in \( \Delta \hat{d}_m \) and \( \Delta Q_m \) are neglected.

In the remaining linear terms, the back-substitution of \( \Delta \hat{d}_m = \hat{d}_m - \langle d \rangle \) and \( \Delta Q_m = Q_m - \langle Q \rangle \) returns back to the original operators, \( \hat{d}_m \) and \( Q_m \). This gives the energy dependence in the \( m \)-th unit cell due to the average dipole moment induced by the off-centre distortion in the \( m \)-th unit cell. Omitting constant terms and plugging the resultant approximated expression of \( H_{mn} \) into (6) gives the decoupled Hamiltonian of the whole crystal. It is a sum of independent (mean-field) Hamiltonians, \( H_{M\Phi}(m) \), of decoupled unit cells, \( H = \sum_m H_{M\Phi}(m) \), additive with respect to different unit cells.

Due to the translational symmetry, the one-cell Hamiltonians are all the same. They do not depend on the cell index \( m \),

\[
H_{M\Phi} = \frac{1}{2M} P^2 + \frac{1}{2} K_0 Q^2 + \Delta \hat{A} + F_0 \langle E + Q \rangle \hat{d} + K_0 D \cdot Q. \tag{8}
\]

Here \( M \) is the mass of the atom \( B \), the vector \( P = \langle P_x, P_y, P_z \rangle \) is its linear momentum conjugated to the off-centre displacement \( Q \). Vectors \( E \) and \( D \),

\[
E = \frac{F}{F_0} \langle d \rangle + \left( \frac{F}{F_0} - 1 \right) \langle Q \rangle, \quad D = \frac{F - F_0}{K_0} \langle d \rangle + \left( \frac{K}{K_0} - 1 \right) \langle Q \rangle, \tag{9}
\]

describe the induced mean field. They act upon the valence electrons and nuclei respectively. In (9), we introduced the inter-cell correlation parameters, \( f = \Sigma_{\alpha\beta} f_{\alpha\beta} \), \( F = \Sigma_{\alpha\beta} F_{\alpha\beta} \), and \( K = \Sigma_{\alpha\beta} K_{\alpha\beta} \). Also, for \( n = 0 \), we assume that \( f_{00} = 0 \), \( F_{00} = F_0 \) and \( K_{00} = K_0 \). One of the mean-field terms, \( F_0 E \cdot \hat{d} \), can be eliminated by the shift transformation, \( Q \rightarrow Q - E \). It changes the Hamiltonian (8) into \( H_{M\Phi} = H_0 + H_{JT} + K_0 (D \cdot E) \cdot Q \) with \( H_0 = \frac{1}{2} (P^2/M + K_0 Q^2) \). As above, the constant terms, the ones that do not include the dynamic operators, \( D, P, \) and \( \hat{d} \), are omitted.

In the octahedron \([BO_6]\), due to the vibronic coupling, an off-centre displacement \( \langle Q \rangle \) of the atom \( B \) induces a low-symmetry redistribution of the electron charge on the six oxygen atoms creating a non-zero electron dipole moment, \( \langle d \rangle \). Vice versa, any low-symmetry distribution of the electric
charge induces an off-centre displacement of the atom $B$. Therefore, expressed by (9), the two contributions to the mean electric field are interdependent and proportional to one another. Consider the commutator of the Hamiltonian, $H_{MF}$, with the linear momentum $P$ of the atom $B$, $[H_{MF}, P]$. It brings to the equation $[H_{MF}, P] = K_0 \langle Q \rangle \hat{d}$. As the average commutator is zero, by averaging this equation, we find the corresponding interdependence, $F_0 \langle d \rangle + K_0 \langle D + \langle Q \hat{d} \rangle \rangle = 0$. Combining it with the equations (9) we come to

$$F \langle d \rangle = -K \langle Q \rangle,$$  \hspace{1cm} (10)

Plugging the equation (10) into the expressions (9), we find both contribution in the mean field, $D$ and $E$, proportional to the average off-centre displacement $\langle Q \rangle$. Correspondingly, the one-cell Hamiltonian (8) takes the form

$$H = H_0 + H_{JT} + L K_0 \langle Q \rangle \cdot \hat{Q}.$$  \hspace{1cm} (11)

As in the high-symmetry case discussed in Section 2, the one-electron Hamiltonian (11) is matrix $9 \times 9$ acting in the basis set of the six HOMO and the three LUMO. Its nine eigenvalues correspond to one-electron energy levels that change adiabatically with the off-centre displacements of the transition-metal $B$. Compared to the one-cell Hamiltonian introduced in Section 2, the only difference of the Hamiltonian (11) is the mean-field term, $L K_0 \langle Q \rangle \cdot \hat{Q}$.

In the case of barium titanate, there are twelve valence electrons populating the hybrid HOMO. The resultant APES is similar to the one introduced in (2) with the addition of the low-symmetry term, $\lambda K_0 \langle Q \rangle \cdot \hat{Q}$.

$$H = \frac{p^2}{2M} + U \langle Q \rangle + \lambda K_0 \langle Q \rangle \cdot \hat{Q}.$$  \hspace{1cm} (13)

Here $U(Q)$ is the same as in Eq.2 and $\lambda = 12L$ with $L$ from Eq.12.

### 3.2. Self-consistent evaluation of order parameters.

At $T = 0K$, the system is locked at the bottom of one of the eight wells, the one deepened by the mean field. The latter is determined by the average value of the off-centre displacement, $\langle Q \rangle$. It has to be evaluated in a self-consistent way, similar to how it is done in the theory of magnetic phase transitions.

At higher temperatures the nuclear motion delocalizes over different wells. In what follows, we consider the two limiting cases: (a) very deep trigonal wells and (b) shallow trigonal minima. The two cases correspond to two significantly different mechanisms of delocalization. In the case (a), when over-the-barrier activation is thermally inaccessible, the delocalization is of a tunnelling nature. In the case (b), when the potential barriers are not very high, it is over-the-barrier activation of Arrhenius type (similar to the Orbach-type relaxation applied to pseudo-spin).

In the case of barium titanate, according to the estimates in Section 2.2, potential barriers between trigonal wells, $\Delta E_{JT} = E_J(110) - E_J(111)$, are of the order of 100 cm$^{-1}$. For the transversal vibration, the one perpendicular to the trigonal axis [111], the energy quantum, $\hbar \omega_{JT}$, is of the same order of magnitude, 100 cm$^{-1}$. Therefore, in BaTiO$_3$ we have the case of a weak-to-moderate coupling, closer to the case (b). In general, in cubic perovskites, we find a wide range of coupling parameters. To some cubic crystals $ABO_3$, one of the two limiting cases applies quite accurately.

### 3.2.1. The tunnelling model for deep trigonal wells.

General theory of tunnelling splitting in Jahn-Teller systems was developed in [31] (see also [24]). The particular case of eight trigonal wells, (the
so-called 8-site model), was considered by Gomez et al. [32]. In the paraelectric phase, when the mean field is zero, \( \langle Q \rangle = 0 \), the one-cell Hamiltonian (13) has cubic symmetry. Its potential energy, the APES, has eight trigonal wells separated by orthorhombic and tetragonal potential barriers discussed in Section 2. If the potential barriers are high enough, \( \Delta E_{JT} \gtrsim \hbar \omega_b \), vibrational motion of the system is locked in one well. Ground state of the unit cell corresponds to eight Born-Oppenheimer states in the wells, \( \langle a \rangle, \langle b \rangle, \langle c \rangle, \ldots, \langle h \rangle \), as labelled in Fig. 1.

When the temperature is low enough, \( kT \lesssim \Delta E_{JT} \), the potential barriers are significantly higher than the energy gaps separating temperature populated states. In this case the set of vibronic states participating in the temperature averaging can be truncated including just the eight vibronic tunnelling states, the ones with the lowest energy. Neglecting tunnelling, if the wells are symmetry equivalent and the ground state is eight-fold degenerate. Tunnelling lifts the eight-fold degeneracy. The ground multiplet splits into two triplets and two singlets, \( A_{ig} + T_{1u} + A_{2u} + T_{2g} \).

The tunnelling Hamiltonian (14) was diagonalized and the tunnelling energy levels were found by Gomez et al. [32]. Energy gaps between the tunnelling energy levels depend on the three overlap integrals, \( \langle a|b \rangle, \langle a|c \rangle, \text{ and } \langle a|g \rangle \). Evidently, for neighbouring wells, the overlap integral \( \langle a|b \rangle \) has dominating value. In a good approximation, the other two, \( \langle a|c \rangle \) and \( \langle a|g \rangle \), can be neglected. In this case the tunnelling multiplet is equidistant. Measured from the ground-state energy level in the infinite-deep wells, the tunnelling energy levels are equidistant,

\[
E(A_{ig}) \approx 3\Gamma, \quad E(T_{1u}) \approx \Gamma, \quad E(T_{2g}) = -\Gamma, \quad E(A_{2u}) = -3\Gamma. \quad (14)
\]

Here \( \Gamma \) is the tunneling parameter,

\[
\Gamma \approx \frac{\hbar \omega_b}{2\pi} \exp \left( -\frac{1}{\hbar} \sqrt{2m \int [U(s) - E_0]ds} \right),
\]

\( \hbar \omega_b \) being the energy quantum of the transversal vibration in a trigonal well, the one perpendicular to the axis [111]. The integral is taken over the arc length \( s \) along the path of steepest descent from the orthorhombic saddle point to the closest trigonal minimum of the APES. In Fig. 4 it is the broken curve. \( U(s) \) is the potential energy (the APES) introduced in Eq.2, and A and B are classical turning points where the system hits the barrier wall.

Using eight tunnelling states as the basis set, the Hamiltonian (13) is represented by the following matrix [32],

\[
H(\alpha) = \Gamma \begin{pmatrix}
3 & -\alpha_x & -\alpha_y & -\alpha_z & 0 & 0 & 0 & 0 \\
-\alpha_x & 1 & 0 & 0 & 0 & -\alpha_x & -\alpha_y & 0 \\
-\alpha_y & 0 & 1 & 0 & -\alpha_z & 0 & -\alpha_x & 0 \\
-\alpha_z & 0 & 0 & 1 & -\alpha_y & -\alpha_x & 0 & 0 \\
0 & 0 & -\alpha_z & -\alpha_y & -1 & 0 & 0 & -\alpha_z \\
0 & -\alpha_z & 0 & -\alpha_y & 0 & -1 & 0 & -\alpha_y \\
0 & -\alpha_y & -\alpha_z & 0 & 0 & 0 & -1 & -\alpha_z \\
0 & 0 & 0 & 0 & -\alpha_x & -\alpha_y & -\alpha_z & -3
\end{pmatrix}.
\]

Here the vector \( \alpha = j(\mathbf{d}) \) is introduced where \( j = \lambda K_0 Q_0^2 / \Gamma \) is the dimensionless correlation constant in terms of the tunnelling parameter \( \Gamma \) and \( \langle \mathbf{d} \rangle \) is the (dimensionless) average dipole moment of electrons.
in one unit cell. The components of \( \mathbf{a} \), namely, \( \alpha_x \), \( \alpha_y \), and \( \alpha_z \), are order parameters of the corresponding ferroelectric phase. They are solutions to the system of the following transcendental equations:

\[
\alpha_i = \frac{j}{\Gamma} \left\langle \hat{a}_i \right\rangle, \quad \left\langle \hat{a}_i \right\rangle = \frac{1}{Z_a} \text{Tr}\left(e^{-H_\alpha/jT} \hat{a}_i \right), \quad Z_a = \text{Tr}\left(e^{-H_\alpha/jT} \right), \quad i = x, y, z. \tag{17}
\]

By substitution, the system of equations (17) can be reduced to three coupled equations,

\[
\Gamma \alpha_i = jkT \frac{\partial}{\partial \alpha_i} \left\{ \ln \text{Tr}\left[e^{-H_\alpha/jT} \right] \right\}, \quad i = x, y, z. \tag{18}
\]

In the lowest-temperature rhombohedral phase, all atoms B are shifted into one of the trigonal wells, say, in the direction \([111]\). In this case, \( \alpha_x = \alpha_y = \alpha_z = \alpha \) and we have just one transcendental equation to solve. The respective minimum is deepened by the mean field. If it is strong enough compared to \( \Gamma \), tunnelling is quenched, and the system is locked in the respective well. Rising temperature weakens the mean field and its locking effect is reduced. The corresponding temperature dependence of the order parameter, \( \alpha \), for different values of correlation parameter \( j = \lambda K_0 Q_0^2 / \Gamma \) is shown in Fig.4. Plugging the resultant value of \( \alpha \) into the expression for the Helmholtz free energy, \( \Phi = -\beta (\ln Z_a) / \beta \) with \( \beta = 1/kT \), we find the free energy of the rhombohedral phase, \( \Phi(111) \).

Similarly, in the orthorhombic phase, all atoms B are “displaced” along the two-fold symmetry axis \([110]\). As there is no minimum on the APES in this direction, this “displacement” should be interpreted as an averaged motion over two near-neighbour wells divided by the orthorhombic potential barrier. In this case, \( \alpha_x = \alpha_y = \alpha \) and \( \alpha_z = 0 \) and again, we have just one equation to solve. Plugging the evaluated value of \( \alpha_x = \alpha_y = \alpha \) and \( \alpha_z = 0 \) into the Helmholtz free energy, we find its value in the orthorhombic phase, \( \Phi(110) \). Solving the equation \( \Phi(111) = \Phi(110) \) for temperature, we can find the \( T_c \) value for the rhombohedral-to-orthorhombic phase transition.

For different ferroelectric phases, the temperature dependence of the Helmholtz free energy is shown in Fig. 5 for the case when \( j = 5 \) chosen as explained below. As above, \( j \) is the dimensionless coupling constant, \( j = \lambda K_0 Q_0^2 / \Gamma \), and \( t = kT / \Gamma \) is the dimensionless temperature in terms of the tunnelling parameter \( \Gamma \). At about \( t = 3.8 \) \( (kT = 3.8 \Gamma) \) the two graphs intersect. Above 3.8\( \Gamma \), the free energy of the orthorhombic phase becomes lower than that of the rhombohedral phase causing the
rhombohedral to orthorhombic phase transition. The respective Curie temperature changes with the inter-cell coupling parameter \( j = J/\Gamma \) are almost linear (Fig. 6).

**Figure 5.** Temperature dependence of the Helmholtz free energy \( \Phi \) (in units of \( \Gamma \)) for the four phases, rhombohedral, orthorhombic, tetragonal, and the paraelectric, at \( j = 5 \). At \( kT < 3.8 \Gamma \), the free energy of the rhombohedral phase is the lowest. With temperature, at \( kT = 3.8 \Gamma \), the free energy of the orthorhombic phase becomes the lowest causing the rhombohedral to orthorhombic phase transition. Above \( kT \approx 4.6 \Gamma \), the tetragonal phase becomes most energy-advantageous.

In the tetragonal phase the atom \( B \) is in tetragonal position, “displaced” along one of the four-fold symmetry axes. Similar to the orthorhombic phase, this “displacement” results from averaging over four close-neighbour trigonal wells by tunnelling through four potential barriers separating them. Therefore, the respective mean-field order parameter can be set as \( a_x = \alpha \) and \( a_y = a_z = 0 \). Plugging it into the Helmholtz free energy, \( \Phi(100) \), and solving the equation \( \Phi(110) = \Phi(100) \), we evaluated the temperature of the orthorhombic-to-tetragonal phase transition shown in Fig. 6. For the same \( j = 5 \) the phase transition takes place at \( t \approx 4.67 \) (\( kT \approx 4.67 \Gamma \)).

**Figure 6.** Temperatures of the two phase transitions, rhombohedral-to-orthorhombic (lower graph, blue) and orthorhombic-to-tetragonal (upper graph, red) versus the dimensionless coupling parameter \( j \).
the orthorhombic-to-tetragonal phase transition changes with \( j \) almost linearly. With the estimated value of the tunnelling parameter, \( \Gamma \approx 38 \text{ cm}^{-1} \), a reasonable fit with the observed temperatures of ferroelectric phase transitions, as shown in Table 2, is achieved at \( j = 5 \).

### Table 2. Calculated values of the two low-temperature phase transitions, rhombohedral-to-orthorhombic \( T_c(I) \) and orthorhombic-to-tetragonal \( T_c(II) \), compared to the experimental values \( T_c(I) = 178\text{K} \) and \( T_c(II) = 278\text{K} \). The percentage errors are evaluated as \( [(T_c - T_{\text{exp}})/T_{\text{exp}}] \times 100\% \).

| \( j \) | 4.6 | 4.7 | 4.8 | 4.9 | 5.0 | 5.1 | 5.2 | 5.3 |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| \( t_1 = \lambda kT_c(I)/\Gamma \) | 3.41 | 3.49 | 3.57 | 3.65 | 3.73 | 3.81 | 3.89 | 3.97 |
| \( T_c(I) \) (in K) | 186 | 191 | 195 | 200 | 204 | 208 | 213 | 217 |
| Percentage error for \( T_c(I) \) | 4 | 7 | 9.5 | 12 | 15 | 17 | 20 | 22 |
| \( t_2 = \lambda kT_c(II)/\Gamma \) | 4.28 | 4.38 | 4.48 | 4.58 | 4.67 | 4.77 | 4.87 | 4.97 |
| \( T_c(II) \) (in K) | 234 | 239 | 245 | 250 | 256 | 261 | 266 | 271 |
| Percentage error for \( T_c(II) \) | 16 | 14 | 12 | 10 | 8 | 6 | 4 | 2.5 |

As one can see from the Table 2, the lower-temperature phase transition is better described with lower values of the mean field parameter \( \lambda \) than the higher-temperature one (with the ratio of about 4.6/5.3). This is quite understandable in view of the larger amplitudes of vibration in the minima at higher temperatures and hence larger intercell interaction of the distortions.

An important side of the tunnelling model is its first-order nature. The above mentioned equations (14) through (18) follow from the first-order perturbation approach to the eight-fold degenerate ground state. In this theory, the small parameter is the tunnelling overlap \( \Gamma \). In the case of barium titanate, as one can see from Fig.5, the tunnelling model fails to provide a reasonable description of the high-temperature phase transition, tetragonal-to-cubic. It could happen by averaging over all eight trigonal wells. This implies a coherent tunnelling through all twelve orthorhombic barriers. Obviously, due to a relatively high entropy factor, the respective probability is too low. An alternative tunnelling path is through the high-symmetry point, \( X = Y = Z = 0 \). In the oxygen octahedron, it corresponds to the on-centre position of the atom of transition metal. This potential barrier is of the order of 0.2 eV = 1600 cm\(^{-1}\). In the case of Ti, the atom mass is 48 u and the 0.2-eV barrier is too high for a reasonable magnitude of the tunnelling energy gap.

#### 3.2.2. The case of relatively shallow trigonal wells.

On the APES, there may be a two-dimensional trough with a relatively weak warping. The latter produces moderately low potential barriers between trigonal minimum points. At the same time, as in the above-mentioned case of barium titanate, the high-symmetry point, \( X = Y = Z = 0 \), may be high in energy, so the first-order tunnelling is impossible. In this case the disorder is achieved by second-order processes through a temperature population of the excited states close in energy to the top of the corresponding potential barrier(s). This is over-the-barrier activation similar to the Arrhenius-type activation of chemical reactions and, also, resembling the Orbach relaxation in magnetic resonance.

The temperature of the ferroelectric phase transition, \( T_c \), is assumed to be of the order of or higher in magnitude than the energy height of the potential barriers, \( kT_c \gtrsim \Delta E_{\text{Jt}} \). Then the hindered rotation of the off-centre atom \( B \) about its on-centre position can be treated in terms of classical mechanics and classical statistical physics. Using the dimensionless parameters introduced in Eq.3, for the average displacement, \( \langle Q \rangle \), we introduce the dimensionless vector \( \overline{Q} = (Q)K_0/F_0 \) with components \( \overline{x} \) and \( \overline{y} \), and
The temperature averaging is over the states of the Hamiltonian (13). Since \( H \) includes the vector \( Q \) as a parameter, it brings to the coupled system of three transcendental equations,

\[
\begin{align*}
\bar{x} &= -t \frac{\partial \ln Z}{\lambda \partial x}, \\
\bar{y} &= -t \frac{\partial \ln Z}{\lambda \partial y}, \\
\bar{z} &= -t \frac{\partial \ln Z}{\lambda \partial z}.
\end{align*}
\]

Here, as above in Eq.17, \( Z \) is the partition function, \( Z = \text{Tr}(e^{-H/kT}) \).

For relatively high temperatures, classical statistics applies, so the partition function can be expressed as the following integral [6]:

\[
Z = \int e^{-H(p,q)/kT} dp dq = ct^{3/2} \int e^{-[u(x,y,z)+\lambda r r]/2} dx dy dz.
\]

Here \( c = \left[ \left( E_{T1}/\omega_0 \right) \sqrt{2\pi} \right] \) is a constant factor with \( \omega_0 = \sqrt{K_0/M} \) and \( E_{T1} = F_0^2/K_0 \), \( t = kT/E_{T1} = kTc_0/F_0^2 \) is the dimensionless temperature, and \( u(x, y, z) \) is the potential energy from Eq.3. In the tetragonal phase the atom \( B \) is displaced in one of the three tetragonal directions, say, along the \( x \) axis. In this case, \( \bar{x} \neq 0 \) and \( \bar{y} = \bar{z} = 0 \). Out of the three equations (19), we are left with just one where the partition sum, \( Z \), is from (20) with the displacement vector \( \bar{r} = (0, 0, 0) \).

For \( \lambda = 0.15 \), the same value as used above in the tunnelling model, the numerical solution of this equation is given in Fig.7. With temperature, the dimensionless displacement, \( \bar{x} \), decreases smoothly to zero at \( t \approx 0.1236 \). In the case of barium titanate with \( F_0^2/K_0 \approx 0.25 \) eV (see the parameter estimate in the Table 1 in Section 2.1), this corresponds to \( kTc \approx 250 \) cm\(^{-1} \approx 359 \) K, reasonably close to the experimental value of 373 K. As distinguished from the low-temperature phase transitions, trigonal-to-rhombohedral and rhombohedral-to-tetragonal, the transformation into the cubic phase is of a second-order.

**4. Discussion.**

Compared to other theories of ferroelectricity, the vibronic approach has two attractive advantages. One is its direct relation to first principles. For a given crystal, it answers the important question about the chemical and structural origin of ferroelectricity. All parameters of the pseudo Jahn-Teller Hamiltonian, the ones introduced in the Eqs.1, 2, and 3, are rigorously defined and can be numerically
evaluated from the corresponding electronic structure. Another important advantage of the vibronic theory is the direct and qualitatively full explanation of the origin of all the experimentally observed properties of the ferroelectric crystals.

The only existent first-principle alternative is a direct calculation of the lowest APES point-by-point as, for example, is described in [17, 18]. However, in this approach the chemical nature of the anharmonicity of the APES, most important for ferroelectricity, is left in the shade of the extensive computer work. The pseudo Jahn-Teller theory reveals the vibronic nature of the anharmonicity and, accompanied with the corresponding group-theoretical analysis, indicates the molecular orbitals responsible for ferroelectricity. In this paper, the main characteristics of cubic perovskites, namely, the local anharmonicity and inter-cell correlation parameter determining the long-range inter-cell coupling were derived from the cooperative pseudo Jahn-Teller effect. For BaTiO₃, the parameters of the theory are in reasonable agreement with the experimental data.

4.1 Order-disorder versus displacive character of ferroelectric phase transitions.

In this paper, following Bersuker [19], we assumed the order-disorder character of ferroelectric phase transitions in cubic perovskites. It results from the local setup of the pseudo Jahn-Teller effect in each unit cell. Supporting this assumption, the most striking example is the off-centre displacement of the atom of Ti in barium titanate observed in the paraelectric phase way above the Curie temperature of the tetragonal-to-cubic phase transition [28]. As accurate measurements indicate, Ti remains displaced closely along [111] directions throughout all of the BaTiO₃ phases. The magnitude of the off-center displacement decreases monotonically by only 13% from 35 to 590 K, showing no steps at the phase transitions [29]. Confirmed by a wide variety of experimental data, including EXAFS [29], optical measurements [34-37], X-ray absorption [38, 39], EPR [40], NMR [41], neutron scattering [28], etc., this observation is in strong disagreement with the theory of displacive phase transitions [4].

At the same time, for phase transitions in barium titanate, a number of experiments seem to support their displacive nature. In particular, the low-frequency (soft) mode was observed in neutron scattering [43], IR absorption [44], hyper-Raman scattering [45], etc. This apparent contradiction has two sides, theoretical and experimental.

4.1.1. The theoretical aspects. Usually, critics of the vibronic approach include its failure to predict the soft mode near the Curie temperature. This argument is wrong. The existence of the soft mode is not rejected by the vibronic theory and follows directly from the temperature dependence of the Helmholtz’ free energy, $\Phi$, with respect to the limiting-phonon TO mode, $[\omega_{\text{eff}}(T)]^2 = (\partial^2 \Phi/\partial q^2)_0$. In this paper, the consideration is limited with the simple version of the mean-field approximation. It does not provide any details about phonon dispersion. Its analysis goes beyond the purpose of the present paper. This study was done in the two-band approach [22, 46-48]. The vibronic hybridization was found responsible for the temperature dependence of phonon frequencies including the temperature drop of the frequency of the limiting-phonon TO mode close to Curie temperature. Its mechanism is in growing population of the low-energy portion of the electron energy band with lowering temperature. This strengthens the pseudo Jahn-Teller effect and reduces the respective curvature, $(\partial^2 \Phi/\partial q^2)_0$.

Extended in this paper, the vibronic approach of Bersuker [19] and the two-band theory of Konsin and Kristoffel [22, 46-48] explore the same physical mechanism of ferroelectricity, namely, the pseudo Jahn-Teller hybridization of electron states. The major difference is in the way the vibronic Hamiltonian is treated. In this paper, the mean-field approximation is used before any Fourier transformation to crystal waves is applied. It addresses the orientation degrees of freedom of the pseudo spin at each unit cell. Therefore, obviously, it provides a better description of the order-disorder phase transitions. In the two-band theory, the mean-field approximation is applied after the Jahn-Teller Hamiltonian is presented in crystal plane-wave form. It operates with crystal lattice modes that are uniform over the whole crystal. Evidently, it is adjusted to describe the displacive transitions.
This raises the question of which way is closer to the real-life situation in cubic perovskites. Introduced above (Section 3.2.1) the tunnelling mechanism of disorder operates with the vibronic pseudo-spin at each metal site. Mathematically, this model is analogous to the one used in magnetic phase transitions in a crystal with non-zero electron spin at each site. No one argues against the order-disorder character of magnetic phase transitions; there is nothing to “displace”. Similarly, as long as the vibronic pseudo spin does not change its magnitude and just changes its orientation when the atom B tunnels from one trigonal well into another, the tunnelling mechanism is of the order-disorder type.

In the rhombohedral phase, all metal atoms are shifted in the same direction. Is it possible that all metal atoms of the crystal coherently hop into a different well creating the displaced orthorhombic phase? The phase transition takes place when the Helmholtz free energy of the two phases becomes equal, \( \Phi(I) = \Phi(II) \). As \( \Phi = U - TS \), the condition of phase equilibrium can be expressed as \( \Delta U = T \Delta S \). When all metal atoms of the crystal coherently hop into another trigonal well, the number of states changes by an order of \( 10^{23} \). Correspondingly, \( \Delta S \) is of the order of \( \ln(10^{23}) = 23\ln(10) = 53 \). For barium titanate, the lowest Curie temperature, \( T = 187 \) K. This gives the right side of the equation, \( T \Delta S \approx 9430 K = 6550 \text{ cm}^{-1} \). From the estimates of the Table 1 (Section 2.1), the orthorhombic potential barrier is of the order of \( \Delta U \approx 100 \text{ cm}^{-1} \), two orders of magnitudes smaller. This means the entropy barrier is too big to be compensated by the left-hand side, \( \Delta U \). Therefore, no coherent transition to another trigonal well can occur.

Interestingly enough, often the entropy argument is used against the vibronic approach in favor of the displacive phase transitions. For tetragonal-to cubic transition in BaTiO\(_3\), from the estimated value of \( \Delta U \) of about \( 0.133 \text{ eV} \approx 1000 \text{ cm}^{-1} \) and \( T = 373 \) K = 260 \text{ cm}^{-1} \), one can evaluate the experimental value, \( \Delta S \approx (1000 \text{ cm}^{-1})/(260 \text{ cm}^{-1}) \approx 4.13 \). In a one-cell disorder, the number of states changes from 1 to 6. This gives \( \Delta S \approx 1.79 \), which is too small compared to the experimental value. The equilibrium can be achieved if we accept the compromising assumption: the number of states changes from 1 to about 62. This means the intercell correlation creates ordered clusters of the size of up to about 10 unit cells [49, 50]. Thus the truth is somewhere in between the two limiting cases of an order-disorder or displacive phase transitions. From this point of view, discussed in the present paper order-disorder phase transition should be understood as rather a simplified description of the real-life case.

4.1.2. The experimental aspects. For the ferroelectric phase transitions in cubic perovskites, the apparent contradiction in experimental manifestations can be explained by their relativity to the means of experimental technique used. Observed with different methods, the same phenomenon can create different impressions. In every unit cell, the vibronic motion has its characteristic time, \( \tau \), and dimension, \( l \). Regarding time, it is the time, \( \tau \), it takes the atom \( B \) to penetrate (by tunneling or hopping) from one trigonal well to another. It is of the order of \( \tau \approx \hbar/\Gamma \). Here, as in Eq.15, \( \Gamma \) is the tunneling parameter. In cubic perovskites, \( \Gamma \) ranges from 0.01 \text{ cm}^{-1} \text{ to } 50 \text{ cm}^{-1} \). Respectively, the characteristic time is from \( \tau \approx 10^{-9} \text{ s} \approx 1 \text{ ns} \) to \( \tau \approx 10^{-13} \text{ s} \approx 0.1 \text{ ps} \). Regarding dimension, \( l \) is the size of one elementary cell where the averaging occurs. For barium titanate, it is of the order of \( l \approx 4 \text{ Å} = 4 \times 10^{-10} \text{ m} = 0.4 \text{ nm} \).

The interpretation of the experimental data has to be related to these two important parameters.

- The observed effect should be attributed to the time scale of the method used. It may be essentially different in different experimental technique. The “time of measurement”, \( \tau_{\text{exp}} \), has to be compared to the time \( \tau \) of the orientation hoping of the metal ion between trigonal wells of the APES [51]. Compared to the characteristic time, the experiment can be short-lasting or long-lasting (Table 3). Discussed by Stern [51], NMR technique can be used as an example. It
measures the nuclear quadruple transitions and motionally averages dynamic displacements that vary in times with characteristic time less than $10^{-8}$ s.

- Also, the observed effect has to be attributed to the characteristic size of the method used, the “experimental length”, $l_{\text{exp}}$. Depending on the experimental technique, the method can be short-range and long-range (Table 3). For example, all optical methods, including IR absorption, hyper-Raman, or Brillouin scattering of light, are long-range methods. Their experimental length, $l_{\text{exp}}$, is of the order of wavelength of the incident or scattered light, $l_{\text{exp}} \sim 10 \text{ nm} \div 10 \mu\text{m}$. This is by several orders in magnitude longer than the crystal characteristic size, $l \approx 4 \text{ Å} = 0.4 \text{ nm}$. Therefore, the long-range methods provide the information averaged over many unit cells. The soft-mode data are correct, however, they do not provide enough reasons to decide (reject or accept) about the order-disorder or displacive nature of the ferroelectric phase transition.

As an alternative technique that can reveal the local disorder, one can use XAFS which is a much faster measurement with a short averaging time, $\tau_{\text{exp}} < 10^{-15}$ s and short range, $l_{\text{exp}} < 0.01$ nm.

### Table 3. Some examples of short-lasting/long-lasting and short-range/long-range experimental techniques.

| Experimental technique used | Short lasting ($\tau_{\text{exp}} \lesssim 10^{-14}$ s) | Long lasting ($\tau_{\text{exp}} \gtrsim 10^{-12}$ s) |
|-----------------------------|----------------------------------------------------|--------------------------------------------------|
| Short-range ($l_{\text{exp}} \lesssim 0.4$ nm) | XAFS | X-ray diffraction Neutron scattering |
| Long-range ($l_{\text{exp}} \gtrsim 10$ nm) | Optical pulse spectroscopy | IR reflectivity NMR Brillouin Scattering Hyper-Raman Scattering |

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