A Local Approach to Solid State Problems: Pseudo Jahn-Teller origin of Ferroelectricity and Multiferroicity

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Abstract

This is a partially review paper in which, in continuation of previous work, it is shown that in perovskite crystals of ABO$_3$ type the spontaneous polarization is triggered by local vibronic interactions, the pseudo Jahn-Teller effect (PJTE). The driving force of the latter is added covalency by distortion, which is essentially of local (chemical) origin. The local origin of polar instability in crystals is confirmed by the theorem of structural instability proved earlier. For crystals of BaTiO$_3$ type local PJT interactions of the metal ion with the oxygen environment results in a peculiar adiabatic potential energy surface (APES) which has eight trigonal [111] type minima, twelve [110] type saddle points between them, six higher in energy [100] type saddle points at the top of the barrier connecting four minima, and a maximum at the cubic symmetry. The temperature dependence of the free energy with this potential explains the origin of all the four phases in such crystals; only the lowest rhombohedral phase is fully ordered, the other two ones at higher temperatures are partially disordered, and the paraelectric phase is fully (three-dimensionally) disordered. For BaTiO$_3$ this picture is confirmed by numerical estimates and ab initio DFT calculations.

An important further development of this theory was reached recently by showing that not only B ions with electronic $d^0$ configurations are subject to the PJTE instability to produce ferroelectricity in perovskite crystals (“the $d^0$ mystery”), but some other specific $d^n$ configurations with unpaired electrons may be dipolar active too, the crystal being thus both magnetic and ferroelectric (multiferroic), and the necessary conditions for such multiferroicity are formulated for the whole $d^0$-$d^n$ variety of perovskites. Moreover, the condition of multiferroicity was shown to depend also on the spin state, high-spin or low-spin, which in conditions of spin crossover leads to a magnetic-ferroelectric crossover that can be manipulated by external perturbations.

1. Introduction. The pseudo Jahn-Teller effects in crystals is of local origin

In any approximate treatment of multi-particle problems a hierarchy of interactions should be taken into account, the strong interactions to be considered first followed by weaker interactions. In ionic dielectric crystals some local interaction may be stronger than long-range forces. In particular, this is true for vibronic coupling of electronic states with local low-symmetry distortions in the Jahn-Teller effect (JTE) and pseudo JTE (PJTE). When such local interactions are stronger than the cooperative forces, many solid state properties are triggered.
first of all by the local effects (that are independent of the translational symmetry). In this sense the approach to such solid state problem should be local: first the local vibronic coupling problem should be solved followed by the cooperative interaction of such local formations. This leads to cooperative JTE (CJTE) and cooperative PJTE (CPJTE) (see, e.g., in [1-3]).

With regard to the JTE, there may be still room for non-local, direct cooperative vibronic coupling called “band JTE” which may take place when the degenerate electronic states are rather delocalized [2, 3]. This is hardly possible for the PJTE; the latter is by essence of local origin. Indeed, consider first the two effects in the simplest case when there are two electronic states, |1⟩ and |2⟩, interacting with one low-symmetry mode Q, a “fingerprint” of the JTE and PJTE illustrated in Fig 1. There are only two parameters to describe the JT instability, the vibronic coupling constant F

\[ F_{12} = \langle 1 | (\partial H / \partial Q) \rangle \langle 2 | \]  

(1)

and the primary force constant,

\[ K_0 = \langle 1 | (\partial^2 H / \partial Q^2) \rangle \langle 1 | \]  

(2)

( \( Q_0 = \frac{F}{K_0} \) and \( E_{JT} = \frac{F^2}{2K_0} \) in Fig. 1a), and only one additional parameter, the energy gap \( \Delta \), is required to describe the instability condition in the PJTE (Fig. 1b),

\[ \Delta < \langle F^2 / K_0 \rangle \]  

(3)
Fig. 1. Energy profiles in a two-level pseudo Jahn-Teller effect (b) versus the Jahn-Teller effect (a) with a single distortion mode. The pseudo crossing in the PJTE case is shown by dashed lines.

At first sight the two pictures are similar indeed, but this similarity does not go very far; it comes out that the differences are more important [4]. First we refer to often encountered in literature two misunderstandings (misrepresentations) of the PJTE that (1) the energy gap $\Delta$ between the interacting states should be small, and (2) the two mixing states belong to the same irreducible representation. They stem from the initial paper of Opik and Pryce [5] who introduced the PJTE to show that a small splitting of the degenerate state, akin to pseudodegeneracy, does not destroy completely the JT instability, provided the inequality (3) is valid. For a long time, the paradigm that $2\Delta$ should be small served as a serious obstacle to the development of this trend. In fact, however, the condition of PJTE instability (3) contains three parameters, so there are no limitations on the values of any one of them, taken separately. With the progress of computational methods it was shown that small $2\Delta$ value is not a necessary condition of the PJTE instability, as it may be compensated in Eq. (3) by larger $F$ values and smaller $K_0$ values. For instance, the conversion of the unstable planar configuration of NH$_3$ to the pyramidal one takes place due to the PJTE coupling to the excited state at $\Delta \sim 14$ eV [6], the PJTE bending of the linear molecules L-M-L with M=Ca, Sr, Ba, and L=Cl, Br, I, takes place at $\Delta \sim 10$ eV [7], and the PJTE ferroelectric distortion in BaTiO$_3$ is produced at the energy gap $\Delta \sim 3.2$ eV (see below in Section 3).

The fact that the PJTE may take place at any reasonable $2\Delta$ values is one of the main points in modern understanding of the PJTE. It extends the number of possible systems subjected to the PJTE to be practically unlimited, including also the systems with the JTE that may, too, be subject to the PJTE. Additionally, the two coupled states in the PJTE may be of any symmetry and, accordingly, the distortion $Q$ can take any direction controlled by the product of symmetries of the two mixing states in the expression (1) of $F$, whereas in the JTE the two degenerate states belong to the same irreducible representation of the symmetry group of the system that limits the possible JTE distortions $Q$.

Most important for the goal of this paper is the *difference in the driving force* that causes the symmetry breakings in these two effects. As seen from Fig. 1a, the derivative of the potential near the point of degeneracy in the JTE is nonzero, meaning a nonzero force causing the
distortion in the Q direction (the force originates from the lower symmetry of the charge distribution in any one of the states of the degenerate term [2]). Contrary to this, in the PJTE there is no distorting force: the first derivative of the potential at the point of highest symmetry is zero (Fig. 1b). So what drives the distortion in the PJTE? The analysis shows [2, 4] that the driving force of symmetry breaking in the PJTE is the added covalence bonding between the near-neighbor atoms by distortion (see also Section 3). Covalency is a net local (chemical) effect dependent on the electronic states of the near-neighbor atoms and facilitated by the PJTE vibronic coupling. In this sense the approach to the solid state problems with PJTE centers should be essentially local, meaning revealing the local PJTE on the centers first and their influence of the crystal properties.

This important statement follows more rigorously from the theorem of lattice instability which proves that the PJTE is the only source of symmetry breaking in polyatomic systems in non-degenerate states [6, 8, 9], and the spontaneous polarization in ferroelectric perovskites is triggered by local polar distortions [10, 11]. Indeed, consider the APES, $E(Q)$, of an ionic cubic crystal ABO$_3$ with perovskite structure near its high-symmetry (cubic) configuration as a function of low-symmetry displacements $Q$ that shift the sublattice of positive (metal B) ions with respect to the negative ones (oxygen atoms) - a limit optical phonon displacement; the displacement of the A atom is ignored. The crystal becomes unstable with respect to polarizing nuclear displacements if the curvature $K$ of the APES in the Q direction at the point of cubic symmetry is negative,

$$K = \left( \frac{\partial^2 E}{\partial Q^2} \right)_0 < 0, \quad \alpha = x, y, z, \quad (4)$$

Putting $E(Q) = \langle \psi_0 | H | \psi_0 \rangle$, where $H$ is the Hamiltonian and $\psi_0$ is the ground-state adiabatic wave function, we get

$$K = \left\langle \psi_0 \left| \frac{\partial^2 H}{\partial Q^2} \right| \psi_0 \right\rangle + 2 \left\langle \psi_0 \left( \frac{\partial H}{\partial Q} \right)_0 \right| \frac{\partial \psi_0}{\partial Q} \right\rangle \quad (5)$$

The first term in (5) is the introduced above $K_0$ magnitude in Eq. (2). Denoting the second one as $K_v$, $K = K_0 + K_v$, we notice that $K_v < 0$. Indeed, presenting $\psi_0'$ in terms of the second-order perturbation theory, we get directly
where the matrix elements in the numerator are the vibronic coupling constants $F_{on}$ introduced in Eq. (1) which together with the energy gap $2\Delta_{0n} = E_n - E_0$ between the mixing states are the main parameters of the PJTE. Therefore $K_v$ is termed vibronic contribution. Thus, being always negative, the $K_v$ term contributes to the instability of the system. If $K_0 > 0$, then the negative term $K_v$ is the only source of instability.

In a series of papers [6, 8, 9] (see also in [2, 3]) the following statement was proved. For any polyatomic system, in the high-symmetry nuclear configuration, where $\left(\frac{\partial E(Q)}{\partial Q}\right)_0 = 0$ (the force-equilibrated configuration in the direction $Q$), the non-vibronic contribution is always positive,

$$K_0 > 0,$$

and, therefore, the vibronic contribution is the only source of instability of any polyatomic system in a non-degenerate state. In case of degenerate states with the JTE, the PJTE produces additional instability, or instability in other (than the JTE) directions. This is the theorem of instability.

For crystal structures the importance of this result is also in the different nature of the two contributions $K_0$ and $K_v$. According to Eq. (2), the primary force constant $K_0$ is a diagonal matrix element of the second derivative with respect to $Q$ which includes a combination of odd-type local distortions of all unit cells over the crystal; reduced to local in-cell displacements $Q^{(m)}$, $K_0$ can be presented as a sum of two contributions [12],

$$K_0^{(a)} = \frac{1}{N} \sum_{m} \langle 0 | \left( \frac{\partial^2 H}{\partial Q^{(m)}_a} \right)^2_0 | 0 \rangle + \frac{1}{N} \sum_{n \neq m} \sum_{a} \langle 0 | \left( \frac{\partial^2 H}{\partial Q^{(m)}_a \partial Q^{(n)}_a} \right)_0 | 0 \rangle. \tag{8}$$

where the first term is the sum of in-cell contributions, and the second term stand for the inter-cell (akin to elastic) interactions. Due to the overwhelming local nature of the chemical bonding in dielectrics, it decreases with the distance, but this decrease is relatively slow, and the respective radius of elastic correlation covers macroscopically large domains in the crystal. $K_0$ is thus a whole-crystal long-range interaction magnitude.

On the contrary, in $K_v$ in Eq. (6) there are only off-diagonal matrix elements of first derivatives of the Hamiltonian, and therefore, translated to local distortions, it does not contain
inter-cell interaction terms. Keeping overlap of atomic wavefunctions of only near-neighbor atoms $|0\rangle$ and $|n\rangle$, we get approximately that the total PJTE vibronic coupling is a sum of local center coupling:

$$K_v^{(a)} = \sum_n \left| \frac{\langle 0 | \left( \frac{\partial H}{\partial Q^a} \right)_0 | n \rangle}{E_0 - E_n (0)} \right|^2$$ (9)

The matrix elements in Eq. (9) are nonzero when the overlap between the corresponding wave function of the near-neighbor atoms of the two sublattices, the ground state of one of them with excited state of the other one ($\psi_0$ and $\psi_n$ in Eq. (6)), increases by the $Q$ displacements.

The local nature of the negative $K_v$ contribution to the curvature means that the instability is essentially of local origin. The long-range interactions presented by $K_0$ are still most important as they play a key role in the realization of the condition of instability $K < 0$ that takes place at $|K_v| > K_0$ (and results in Eq. (3) in a two-level approximation). The trigger mechanism of spontaneous polarization of the crystal is thus of local PJTE origin directly related to its atomic (electronic) structure, but the magnitude of local distortion and the crystal polarization depends also on the long-range interactions. In other words, the long-range interactions $K_0$ by themselves, without the negative local contribution $K_v$ (without the added covalency[2]) cannot produce the spontaneous polarization of the crystal, whereas $|K_v|$ may be too small yielding just the weak PJTE without instability or the local instability by itself may be not strong enough to overcome the rigid lattice. $K_0$ and $K_v$ depend also on the third ion A in the perovskite (Ba in BaTiO$_3$) as it defines the size of the unit cell which influences all the Ti-O interactions (see below).

### 2. PJTE origin of ferroelectricity in perovskite crystals

The theoretical investigation of the origin of ferroelectricity and ferroelectric phase transitions has already a long history (see [13] and references therein). Below we describe the modern aspects of our vibronic (PJTE) theory of this phenomenon. As it follows from the theorem of instability, the ferroelectric displacements in a cubic perovskite crystal structure ABO$_3$ are
triggered by the local PJTE coupling in the transition-metal center. Therefore, we start with the Hamiltonian of one unit cell in the high-symmetry cubic configuration. Consider the octahedral fragment of the unit cell centered at the transition metal atom B (red circle in Fig. 2). It is surrounded by six oxygen atoms (blue circles in Fig. 2). Cation atoms A are not shown.

For the octahedral fragment \([\text{BO}_6]^8\) shown in Fig. 2, in the MO LCAO presentation (e.g., see [14]) the highest occupied MO (HOMO) are formed by the atomic 2\(p_\pi\) orbitals of the six oxygen atoms. They belong to the representations \(T_{1u}, T_{2u},\) and \(T_{1g}\) of the octahedral symmetry group and are denoted in Fig. 3 by \(t_{1u}, t_{2u},\) and \(t_{1g}\), respectively. The lowest unoccupied MO (LUMO) are \(t_{2g}(3d)\) orbitals of the transition metal: \(|yz(B)\rangle, |xz(B)\rangle,\) and \(|xy(B)\rangle\) (Fig. 3). In the regular cubic configuration, these HOMO-LUMO orbitals are orthogonal and do not participate in the Ti—O bonding (the bonding is realized via the inner \(\sigma\) orbitals and ionic interactions). Obviously, any off-center displacement of the atom B lowers the cubic symmetry and makes their overlap nonzero. Fig. 4 illustrates this effect for the orbital \(|yz(Ti)\rangle\). This orbital overlap means additional covalence in the Ti—O bonding, thus explaining the origin of the PJTE as due to added covalence. It is the driving force in the vibronic coupling (PJTE) origin of the local dipolar instability that produces the ferroelectric polarization of the crystal.
Fig. 2. (Color online) The octahedral fragment of the perovskite crystal structure ABO$_3$ with the transition metal atom B at the center (red) and six oxygen atoms (blue) at the apexes of the octahedron. The letters a, b, c, … denote the induced by the PJTE off-center positions of the atom B in the eight wells of the APES.
Fig. 3. (Color online). The energy level diagram for the octahedral cluster TiO$_6^{8-}$. The HOMO $t_{1u}$ and $t_{2u}$ (mostly oxygen) and LUMO $t_{2g}$ (mostly titanium) levels that are vibronic coupled in the PJTE are shown in red.
Fig. 4. Illustration to the added covalence in the PJTE: the net overlap of the $3d$ orbital $|T_2u(Ti)y\rangle$ with $\pi$ orbitals of the surrounding oxygen atoms (shaded) is zero when the metal ion is at the center and becomes non-zero in its $y$-direction off-center displacement inducing additional covalence bonding Ti—O.

With the fully occupied HOMO, the ground state is $A_{1g}$. Since the three Cartesian coordinates of the central atom, $Q_x$, $Q_y$, and $Q_z$, transform as $T_{1u}$, the general PJT vibronic coupling problem is $(A_{1g} + T_{1u}) \otimes t_{1u}$, where $T_{1u}$ is the excited state formed by the one-electron excitation HOMO $\rightarrow$ LUMO ($t_{1u} \rightarrow t_{2g}$). There may be many such excitations, so the problem is better formulated as the vibronic coupling of the six HOMOs $t_{1u}$ and $t_{2u}$ to the three LUMOs $t_{2g}$ via the dipole-active displacements of the central atom, $Q_x$, $Q_y$, and $Q_z$.

With the linear vibronic coupling included, the Hamiltonian of the PJTE becomes as follows [2, 3, 12]:

$$
$$
Here the HOMO-LUMO energy gap is denoted by $2\Delta$ (the energy levels of the HOMO $t_{1u}$ and $t_{2u}$ are approximately degenerate) and the vibronic coupling constant is

$$F = \left( 2p_z (O) \left( \frac{\partial H}{\partial Q} \right) \right) \left( 3d_{xy} (Ti) \right).$$  \hspace{1cm} (11)

The particular form of the matrix Hamiltonian (14) follows from symmetry considerations. It has the following nine eigenvalues:

$$\epsilon_1 = \sigma_x, \quad \epsilon_2 = -\sigma_x, \quad \epsilon_3 = \sigma_y, \quad \epsilon_4 = -\sigma_y, \quad \epsilon_5 = \sigma_z, \quad \epsilon_6 = -\sigma_z, \quad \epsilon_7, \epsilon_8, \epsilon_9 = -\Delta.$$  \hspace{1cm} (12)

Here $\sigma_i = \sqrt{\Delta^2 + 2F^2 (Q_i^2 - Q_{i'}^2)}$ and $Q^2 = Q_x^2 + Q_y^2 + Q_z^2$. For eigenvalues $\epsilon_1$, $\epsilon_2$, and $\epsilon_3$, the corresponding eigenvectors are:

$$\begin{align*}
\psi_1^+ &= N_1 \left( \Delta + \sigma_x, \ 0, \ 0, \ 0, \ FQ_z, \ FQ_y, \ 0, \ FQ_z, \ -FQ_y \right), \\
\psi_2^+ &= N_2 \left( \Delta - \sigma_x, \ 0, \ 0, \ 0, \ FQ_z, \ FQ_y, \ 0, \ FQ_z, \ -FQ_y \right), \\
\psi_3^+ &= N_3 \left( 0, \ 0, \ 0, \ 0, \ Q_y, \ -Q_z, \ 0, \ Q_y, \ Q_z \right),
\end{align*}$$  \hspace{1cm} (13)

with the normalization factors $N_1 = \left[ 2\sigma_x (\sigma_x + \Delta) \right]^{1/2}$, $N_2 = \left[ 2\sigma_x (\sigma_x - \Delta) \right]^{1/2}$, and $N_7 = \left[ 2(Q_x^2 - Q_{i'}^2) \right]^{1/2}$. The remaining six eigenvectors can be obtained from Eq. (17) by symmetry operations of the cubic group.

Populated with 12 electrons, the lowest one-electron orbital energy levels (16) generate the ground-state adiabatic potential energy surface (APES) reported in the first paper on the vibronic theory in 1966 [10]:

$$U(Q) = \frac{1}{2} K_0 Q^2 - 2 \left[ \sqrt{\Delta^2 + 2F^2 (Q_i^2 - Q_{i'}^2)} + \sqrt{\Delta^2 + 2F^2 (Q_y^2 - Q_z^2)} + \sqrt{\Delta^2 + 2F^2 (Q_z^2 - Q_x^2)} \right].$$  \hspace{1cm} (14)
Here we added the elastic energy of the off-center distortion \( \frac{1}{2} K_0 Q^2 \), where \( K_0 \), as above, is the respective primary force constant. It is due to the \( \sigma \) bonds and other (electrostatic) interactions between the oxygen and titanium atoms. The APES (14) includes three parameters, \( K_0, \Delta, \) and \( F \), and three nuclear coordinates, \( Q_x, Q_y, \) and \( Q_z \). By introducing dimensionless \( u, \delta, x, y, \) and \( z \),

\[
U = u \frac{F^2}{K_0}, \quad \Delta = \delta \frac{F^2}{K_0}, \quad Q_x = x \frac{F}{K_0}, \quad Q_y = y \frac{F}{K_0}, \quad Q_z = z \frac{F}{K_0},
\]

we reduce the number of relevant parameters to just one, \( \delta \). The dimensionless APES is \( r^2 = x^2 + y^2 + z^2 \):

\[
u(x, y, z) = \frac{1}{3} r^2 - 2 \left[ \sqrt{\delta^2 + 2 \left( y^2 + z^2 \right)} + \sqrt{\delta^2 + 2 \left( x^2 + z^2 \right)} + \sqrt{\delta^2 + 2 \left( x^2 + y^2 \right)} \right].
\]

Under condition \( 0 \leq \delta \leq 8 \), or

\[
\Delta < \frac{8F^2}{K_0},
\]

the APES (14), [or its dimensionless version (16)], has eight trigonal minimum points, \( r_0(1, -1, -1), \ r_0(1, 1, 1), \ r_0(-1, 1, 1), \ r_0(-1, -1, 1), \ r_0(1, -1, 1), \ r_0(1, 1, -1), \ r_0(-1, 1, -1), \) and \( r_0(-1, -1, -1) \). In Fig.1, they are labeled \( a, b, c, d, e, f, g, \) and \( h \), respectively. At these points we have \( r_0 = \frac{1}{2}(64 - \delta^2)^{1/2} \) and the stabilization energy \( E_{JT}(111) = \frac{3}{8}(8 - \delta^2) \). Returning back to the variables (19), we have

\[
Q_0 = \frac{F}{2K_0} \sqrt{64 - \delta^2}, \quad E_{JT}(111) = \frac{3F^2}{8K_0} \left( 8 - \delta \right)^2.
\]

The inequality \( 0 \leq \delta \leq 8 \) or (17) is the condition of instability. When the energy gap is larger than \( 8F^2/K_0 \), or \( \delta > 8 \), the vibronic coupling is not strong enough to provide the dipole instability. In this case, there is just one stable configuration, the on-center position of the atom B, and ferroelectricity is impossible.

The curvature of the APES at the minimum points follows from the eigenvalue problem for the matrix of second derivatives of \( u(x, y, z) \) in (16). 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 respective curvature is \( k_A = \frac{1}{44} (64 - \delta^2) \). The two-fold mode corresponds to transverse vibrations perpendicular to the direction \([111] \). Its curvature is \( k_E = \frac{1}{4} k_A \). In the variables (15) the respective expressions are

\[
K_A = \frac{1}{44} K_0 \left( 64 - \delta^2 \right), \quad K_E = \frac{1}{4} K_A.
\]
In addition to the minima the APES (14) has two types of saddle points: orthorhombic and tetragonal. The twelve orthorhombic saddle points, $Q_1(1, 1, 0)$, $Q_1(1, -1, 0)$, $Q_1(-1, 1, 0)$, $Q_1(-1, -1, 0)$, $Q_1(1, 0, 1)$, $Q_1(1, 0, -1)$, $Q_1(-1, 0, 1)$, $Q_1(-1, 0, -1)$, $Q_1(0, 1, 1)$, $Q_1(0, 1, -1)$, $Q_1(0, -1, 1)$, and $Q_1(0, -1, -1)$ with

$$Q_1 = \frac{F}{3K_0} \sqrt{64 - \delta^2} = \frac{2}{3} Q_0,$$

$$E_{JT}(110) = 0.34 \frac{F^2}{K_0} (8 - \delta)^2 = 0.91 E_{JT}(111).$$

The orthorhombic saddle points separate the eight trigonal wells from one another with potential barriers

$$\Delta E_{JT} = E_{JT}(111) - E_{JT}(110) = 0.09 \frac{F^2}{K_0} (8 - \delta)^2.$$  

The six tetragonal saddle points are at $Q_2(1, 0, 0)$, $Q_2(-1, 0, 0)$, $Q_2(0, 1, 0)$, $Q_2(0, -1, 0)$, $Q_2(0, 0, 1)$, and $Q_2(0, 0, -1)$ with

$$Q_2 = \frac{F}{2K_0} \sqrt{2(64 - \delta^2)} = Q_0 \sqrt{2},$$

$$E_{JT}(100) = \frac{F^2}{4K_0} (8 - \delta)^2 = \frac{2}{3} E_{JT}(111).$$

Available experimental and \textit{ab initio} calculations data allow us to estimate the APES parameters for BaTiO$_3$, at least by order of magnitude. From the three independent parameters that control the local PJTE displacements, the energy gap $2\Delta$ to the PJT-active excited state is relatively well known, $2\Delta = 3.25$ eV. Another parameter can be obtained from the experimental value of the off-center displacement of the Ti ion in the trigonal minimum of the APES, $Q_0 \approx 0.11$ Å. It is a function of the vibronic coupling constant $F$ and the primary force constant $K_0$. The third independent parameter can be obtained from the value of the PJT stabilization energy in the APES minimum $E_{JT}(111)$. From the \textit{ab initio} calculations (see, e.g., Section 4) we get $\Delta E_{JT}(\text{calc}) \approx 0.3$ eV while from XAFS experiments $\Delta E_{JT}(\text{exp}) \approx 0.2$ eV [15]. Notably, the two values do not differ essentially, and the origin of their difference is quite understandable: the calculated value is determined from the crystal ferroelectric phase where the distortion is enhanced by the cooperative interactions, whereas the XAFS experiments are performed on the paraelectric phase, and hence reflect just the local distortion. For our local model the latter value is more appropriate.

Another option to involve experimental data is to exploit vibrational frequencies. In particular, in the APES minimum the transversal vibration $\hbar \omega_k$ (the one perpendicular to the axis [111]) may be assumed to represent approximately the soft mode behavior at low temperatures.
The usual estimate \[h\omega_e \sim 100 \text{ cm}^{-1}\]. From this value, applying Eqs.(14) and (18), we find the other parameters. The two versions of the numerical estimate of all the relevant parameters are given in the Table 1.

**Table 1.** Numerical values of the PJTE parameters obtained from the comparison of experimental data with the calculated APES, given in two versions based on two sets of data [12].

| Main parameters | Version I \[E_{JT}(111) = 0.2 \text{ eV}\] | Version II \[h\omega_e = 100 \text{ cm}^{-1}\] |
|-----------------|---------------------------------|---------------------------------|
| \(K_0\)        | 163 eV/Å\(^2\)                 | 114 eV/Å\(^2\)                 |
| \(h\omega_0\)  | 963 cm\(^{-1}\)                | 805 cm\(^{-1}\)                |
| \(F\)          | 6.37 eV/Å                       | 5.17 eV/Å                       |
| \(\delta\)     | 6.54                            | 6.94                            |
| \(E_{JT}(111)\) | 0.2 eV                          | 0.098 eV                        |
| \(h\omega_E\)  | 277 cm\(^{-1}\)                | 100 cm\(^{-1}\)                |
| \(E_{JT}(110)\) | 0.1804 eV                       | 0.0876 eV                       |
| \(\Delta E_{JT} = E_{JT}(110) - E_{JT}(111)\) | 150 cm\(^{-1}\)             | 78 cm\(^{-1}\)                |

We see that, in spite of essentially different experimental data used in the two estimates, the numerical values are quite reasonable and rather consistent (within the expected orders of magnitude). With these parameters we can verify the PJTE criterion of instability \(\Delta < 8F^2/K_0\) in Eq. (17). In both versions of Table 1 the electron energy gap \(2\Delta = 3.25\text{eV}\) is less than the PJT stabilization energy \(16F^2/K_0\) equal to 3.38 eV and 3.74 eV in the versions I and II, respectively. This result shows that the PJTE is not limited to narrow energy gaps between interacting states, and it is feasible for perovskite systems. On the other hand, the condition of instability may be very restricting, which is why it is not realized in other similar systems (see Section 4). From these estimates we see that the performed above approximate evaluation of the PJTE yields a reasonable physical picture of the phenomenon of ferroelectricity compatible with the experimental observations.

Note that the essentially anharmonic APES (14) is obtained without involving the anharmonic terms in the Hamiltonian; only linear terms of vibronic coupling are included in Eq. (10). On the other hand, it was shown (Section 4) that just anharmonicity included in the Hamiltonian up to forth-order terms, does not produce the eight-minimum potential surfaces. Thus, with its eight trigonal wells, twelve orthorhombic saddle points, and six tetragonal saddle points, the APES (14) is a sole result of the PJTE. By the PJT hybridization of the ground and
excited electronic states it generates the so-called “vibronic anharmonicity” [2, 3] which is much more ample than the singlet anharmonicity introduced directly in the Hamiltonian.

3. Origin of multiferroicity and magnetic-ferroelectric crossover

Coexistence of ferroelectric and magnetic properties (multiferroicity) implies that the ferroelectric crystal, which is a dielectric, has also a nonzero magnetic moment, meaning unpaired electrons. In the ferroelectric BaTiO$_3$ with perovskite ABO$_3$ structure the $d^0$ configuration of the Ti$^{4+}$ ion has no unpaired electrons, and attempts to obtain ferroelectricity in perovskites with $d^n$, $n>0$, transition metals B ions were unsuccessful for a long time. This prompted some authors to term the situation as a “$d^0$ mystery” for ferroelectrics. However, more recently quite a number of ferroelectrics-multiferroics, mostly perovskites with configurations $d^3-d^7$, were obtained and studied [16, 17]. The origin of these special properties of perovskite ferroelectrics with $d^n$ configurations does not follow directly from displacive theories, and so far had no general explanation. In this paper we show that the vibronic (PJTE) theory of ferroelectricity, outlined above, explains also directly the origin of perovskite multiferroics with proper ferroelectricity and formulates the necessary conditions that ABO$_3$ perovskites with a magnetic $d^n$ configuration of the B ion may be ferroelectric. Moreover, we show also that the multiferroics conditions that emerge from the PJTE for $d^n$ ions with $n=3$, 4, 5, 6, and 7, are directly influenced by the well known transition metal high-spin/low-spin crossover, resulting in the coexistence of three phenomena: ferroelectricity (FE), magnetism (M), and spin crossover (SCO). This, in turn, leads to a quite novel phenomenon: magnetic-ferroelectric (multiferroics) crossover (MFCO), creating a rich variety of possible magnetoelectric and related effects [18].

The typical molecular-orbital (MO) energy scheme for an octahedral cluster BO$_6^{8-}$ in the approximation of linear combinations of atomic orbitals is shown above in Fig. 2 with the MO electron population of the $d^0$ configuration, e.g., when B=Ti. The highest occupied MO (HOMO) in this case is $t_{1u}$ which is a threefold degenerate odd-parity (ungerade) linear combination of mostly oxygen $p$ orbitals, while the lowest unoccupied MO (LUMO) is $t_{2g}$, mostly atomic three $d$, orbitals of the transition metal ion B, and the next excited MO is the double degenerate one $e_g$ (the non-bonding oxygen $b_{1g}$ MO is not shown as irrelevant). For the $d^0$ case the HOMO configuration is thus $(t_{1u})^6(t_{1u\downarrow})^3(t_{1u\uparrow})^3$, where the arrows up and down indicate the two spin
states; the energy term of this configuration is $^{1}A_{1g}$. The excited state with opposite parity is formed by the one-electron $(t_{1u} \uparrow) \rightarrow (t_{2g} \uparrow)$ or $(t_{1u} \uparrow) \rightarrow (e_{g} \uparrow)$ excitation resulting in the lowest excited ungerade term $^{1}T_{1u}$ at the energy gap $2\Delta$. The PJTE vibronic coupling constant under the polar displacements of the B atom along [111] is given above in Eq. (11), while the condition of instability $\Delta<8F^{2}/K_{0}$ follows from Eqs. (17).

For the $d^{1}$ configuration of the B ion instead of the $d^{0}$ the HOMO becomes $(t_{1u} \downarrow)^{3}(t_{1u} \uparrow)^{3}(t_{2g} \uparrow)^{1}$ with the term $^{2}T_{2g}$, and LUMO (taken into account Hund’s rule) is $(t_{1u} \downarrow)^{2}(t_{1u} \uparrow)^{3}(t_{2g} \uparrow)^{2}$ with the lowest excited ungerade term $^{4}T_{1u}$. Hence the two closest terms of different parity (that otherwise could mix under nuclear displacements to produce the PJT dipolar distortion), possess different spin multiplicity, and hence they do not mix by the vibronic coupling; the latter does not contain spin operators [1-3]. In principle, there may be higher in energy electronic configurations of opposite parity with the same spin as the ground state one, but they are at much larger energy gaps $\Delta$, and therefore hardly satisfying the condition of instability (17) (numerical estimate show that the condition (17) is very limiting [41]). A similar picture emerges for $d^{2}$ configurations for which the two lowest terms of opposite parity are $^{2}T_{2g}$ and $^{5}T_{1u}$ (see Table 2).

The situation changes for $d^{3}$. Indeed in this case the HOMO is $(t_{1u} \downarrow)^{3}(t_{1u} \uparrow)^{3}(t_{2g} \uparrow)^{3}$ with the ground state term $^{4}A_{1g}$, and in the low-spin conditions of the strong ligand fields (large $t_{2g}-e_{g}$ separation in Fig. 3, see, e.g., [14]) the LUMO is $(t_{1u} \downarrow)^{2}(t_{1u} \uparrow)^{3}(t_{2g} \uparrow)^{1}(t_{2g} \downarrow)^{1}$ with the lowest ungerade term $^{4}T_{1u}$. Therefore for $d^{3}$ configurations (e.g., Mn$^{4+}$) in sufficiently strong ligand fields the situation becomes again favorable for the PJTE and polar distortions, but in this case, distinguished from the $d^{0}$ case, the system possess also a magnetic moment created by three unpaired electrons. However, if the ligand field is weak and the separation $t_{2g}-e_{g}$ is small, the high-spin arrangement of the excited electronic configuration takes place, and the excitation electron occupies the $e_{g} \uparrow$ orbital instead of $t_{2g} \downarrow$; the LUMO configuration under Hund’s rule becomes $(t_{1u} \downarrow)^{3}(t_{1u} \uparrow)^{3}(t_{2g} \uparrow)^{3}(e_{g} \uparrow)^{1}$ with the lowest ungerade state $^{6}T_{1u}$. Here again there is no PJTE on dipolar distortions and no ferroelectric instability. In this way we considered all the $d^{n}$ configurations with $n=0, 1, 2, \ldots, 10$, shown in Table 2.

It follows from this table that according to the PJTE only B ions with configurations $d^{3}$-low-spin, $d^{4}$-low-spin, $d^{5}$-low-spin and high-spin, $d^{6}$-high-spin and intermediate-spin, $d^{7}$-high-spin, $d^{8}$, and $d^{9}$ can, in principle, produce multiferroics, provided the criterion of instability (8) is
fulfilled. Transition metal ions B with configurations $d^1$, $d^2$, $d^3$-high-spin, $d^4$-high-spin, $d^5$-low-spin, $d^6$-low-spin, and $d^{10}$ are not expected to produce multiferroics under this mechanism. Experimentally obtained perovskite multiferroics with such B ions, for example, Mn$^{4+}(d^3)$, Cr$^{3+}(d^3)$, Mn$^{3+}(d^4)$, Fe$^{3+}(d^5)$, Fe$^{2+}(d^6)$, Co$^{2+}(d^7)$, etc. [16, 17], fit well with the conclusions of Table 2; there are no multiferroics with $d^0$, $d^1$, $d^2$, and $d^{10}$ configurations.

Table 2. Necessary conditions that ABO$_3$ perovskites with the electronic $d^n$ configuration of the B ion possess both ferroelectric and magnetic properties simultaneously [18]; EC=electronic configuration, GS = ground state, LUES = lowest ungerade excited state, FE = ferroelectric, MM = magnetic, MF = multiferroic, LS = low-spin, HS = high-spin; IS = Intermediate spin; LS* and HS* are two spin configurations of $d^3$ in the one-electron excitation. $(t_{1u})^6 = (t_{1u} \downarrow)^3(t_{1u} \uparrow)^3$; $(t_{1u})^5 = (t_{1u} \downarrow)^2(t_{1u} \uparrow)^3$; $(t_{2g})^6 = (t_{2g} \uparrow)^3(t_{2g} \uparrow)^3$; $(e_g)^4 = (e_g \uparrow)^2(e_g \downarrow)^2$.

| $d^n$ | Example | HOMO EC and GS term | LUMO EC and LUES term | FE | MM | MF |
|-------|---------|----------------------|-----------------------|----|----|----|
| $d^0$ | Ti$^{4+}$ | $(t_{1u})^6, A_g$ | $(t_{1u})^3(t_{2g} \uparrow)^1, T_{1u}$ | yes | no | no |
| $d^1$ | Ti$^{3+}$, V$^{4+}$ | $(t_{1u})^6(t_{2g} \uparrow)^1, 2T_{2g}$ | $(t_{1u})^5(t_{2g} \uparrow)^2, 2T_{1u}$ | no | yes | no |
| $d^2$ | V$^{3+}$, Cr$^{4+}$ | $(t_{1u})^6(t_{2g} \uparrow)^2, 3T_{2g}$ | $(t_{1u})^5(t_{2g} \uparrow)^3, 3T_{1u}$ | no | yes | no |
| $d^3$, LS | Cr$^{3+}$, Mn$^{4+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3, 4A_g$ | $(t_{1u})^5(t_{2g} \uparrow)^3(t_{2g} \downarrow), 4T_{1u}$ | yes | yes | yes |
| $d^3$, HS | Mn$^{3+}$, Fe$^{4+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3, 4A_g$ | $(t_{1u})^5(t_{2g} \uparrow)^3(e_g \uparrow)^1, 5T_{1u}$ | no | yes | no |
| $d^4$, LS | Mn$^{4+}$, Fe$^{3+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3(t_{2g} \downarrow), 3T_{2g}$ | $(t_{1u})^5(t_{2g} \uparrow)^3(t_{2g} \downarrow), 3T_{1u}$ | yes | yes | yes |
| $d^4$, HS | Mn$^{3+}$, Fe$^{3+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3(e_g \uparrow), 5T_{2g}$ | $(t_{1u})^5(t_{2g} \uparrow)^3(e_g \uparrow)^2, 5T_{1u}$ | no | yes | no |
| $d^5$, LS | Mn$^{2+}$, Fe$^{4+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3(t_{2g} \downarrow), 2T_{2g}$ | $(t_{1u})^5(t_{2g} \downarrow)^6, 2T_{1u}$ | yes | yes | yes |
| $d^5$, HS | Fe$^{3+}$, Co$^{3+}$ | $(t_{1u})^6(t_{2g} \uparrow)^3(e_g \uparrow)^2, 6A_g$ | $(t_{1u})^5(t_{2g} \downarrow)^4(e_g \uparrow)^2, 6T_{1u}$ | yes | yes | yes |
| $d^6$, LS | Fe$^{2+}$, Co$^{3+}$ | $(t_{1u})^6(t_{2g} \uparrow)^1, A_g$ | $(t_{1u})^5(t_{2g} \downarrow)^6(e_g \uparrow)^1, 7T_{1u}$ | no | no | no |
| $d^6$, IS$_1$ | $(t_{1u})^5(t_{2g} \uparrow)^3(e_g \downarrow)^3, 3T_{1u}$ | $(t_{1u})^5(t_{2g} \downarrow)^6(e_g \uparrow)^1, 3T_{1u}$ | yes | yes | yes |
| $d^6$, IS$_2$ | $(t_{1u})^5(t_{2g} \downarrow)^4(e_g \uparrow)^2, 3T_{1u}$ | $(t_{1u})^5(t_{2g} \downarrow)^5(e_g \uparrow)^2, 3T_{1u}$ | no | yes | no |
| $d^6$, HS | Fe$^{3+}$, Co$^{3+}$ | $(t_{1u})^6(t_{2g} \downarrow)^4(e_g \uparrow)^2, 5T_{2g}$ | $(t_{1u})^5(t_{2g} \downarrow)^5(e_g \uparrow)^2, 5T_{1u}$ | yes | yes | yes |
| $d^7$, LS | Co$^{2+}$, Ni$^{3+}$ | $(t_{1u})^6(t_{2g} \uparrow)^1, 2E_g$ | $(t_{1u})^5(t_{2g} \downarrow)^6(e_g \uparrow)^2, 4T_{1u}$ | no | yes | no |
Of special importance is also the fact that some $d^n$ ions with $n=3$, 4, 5, 6, and 7, dependent on the ligands of the octahedral environment, may produce two types of magnetic centers, high-spin (HS) and low-spin (LS), and in $d^6$ case there may also intermediate spin (IS) states ($d^3$ has two spin configurations in the one-electron excitation). According to our analysis, only $d^5$ systems follow the necessary condition of potential multiferroics in both spin states, but the PJTE condition of instability (8) and the magnetic moments are different in these two cases. For $d^3$, $d^4$, $d^6$, and $d^7$ ions only one of the two spin states may serve as a candidate of potential multiferroics. On the other hand, in many cases the two spin states are close in energy producing a well known phenomenon of transition metal spin crossover (SCO), in which case the system can be relatively easily transferred from one spin state to another by external perturbations like heat, light, and magnetic fields (for reviews see [19]). Since, as shown above, the change of the spin state changes also the ferroelectric state, the SCO is simultaneously a magnetic-ferroelectric (multiferroic) crossover (MFCO). This coexisting magnetic, ferroelectric, and SCO phenomena opens a variety of new possibilities to manipulate the properties of the system with exciting novel functionalities to electronics and spintronics. Here are several examples:

1. For $d^3$ and $d^4$ (Cr$^{3+}$, Mn$^{4+}$, Mn$^{3+}$, Fe$^{4+}$, etc.) ferroelectrics in the LS state in conditions of MFCO, magnetic fields facilitate the LS$\rightarrow$HS transition that destroys the ferroelectricity (and multiferroicity), while an electric field in the HS non-ferroelectric state may transfer the system to the ferroelectric (multiferroic) LS state, thus realizing electric demagnetization;

2. For $d^5$ ferroelectrics in conditions of MFCO, if the ferroelectricity is (most probable) different in the two spin states, an electric field may change the spin state (electric magnetization or demagnetization);
3. For $d^6$ and $d^7$ (Fe$^{2+}$, Co$^{3+}$, Co$^{2+}$, Ni$^{3+}$, etc) in the non-ferroelectric LS state under conditions of MFCO, magnetic fields facilitates the LS→HS transition that induces ferroelectricity and hence multiferroicity in a strong magnetoelectric effect (the $d^6$ LS state is nonmagnetic); in the non-ferroelectric LS state in MFCO conditions, an electric field may transfer the system to the multiferroic state (electric magnetization);

4. The SCO phenomenon is well known to be influenced also by stress, heat, light, and cooperative effects in crystals [19], hence these perturbations can be used to manipulate the MFCO and all the consequent properties including those mentioned above. The dependence of the MFCO on pressure adds a ferroelastic order to the magnetic and ferroelectric ones;

5. There is already a long history of attempts to use transition metal SCO systems as units of magnetic bistability; the difficulty is in the fast relaxation (short lifetime) of the higher in energy spin state [20]. By choosing a system in the MFCO condition, one can increase the lifetime of the excited dipolar (multiferroic) state by applying an external electric field.

6. An important feature of the revealed MFCO is that it is of local origin and hence it does not necessarily require strong cooperative interactions, meaning that, in principle, it may take place as a magnetic-dipolar effect in separate molecular systems, clusters, thin films, etc., provided the condition of instability (17) takes place.

4. Further comparison with experimental data

One of the main features of the vibronic theory of ferroelectricity under consideration as compared with other approaches is that it yields a direct and qualitatively full explanation of the origin of all the experimentally observed properties of the ferroelectric crystals [21-36]. Below we list several basic properties that so far can be explained exclusively by the vibronic theory.

1. Off-center displacement of the B (metal) atom in the paraelectric phase. This property is confirmed by a variety of experimental data mentioned above, noticeable EXAFS [29-31], optical measurements [22-24, 32], X-ray absorption [25,26], EPR experiments [27, 28], NMR [33, 34], neutron scattering [35], etc., in disagreement with all displacement theories in which the metal off-center displacement occurs as a result of the phase transition. Not only is the Ti ion displaced along the [111] type direction in the paraelectric phase where the averaged symmetry
is cubic, but it is displaced in this direction in the tetragonal phase where the crystal symmetry and the macroscopic polarization are tetragonal [35]. In the vibronic theory the off-center displacement of the B atom along [111] is due to the local PJTE that is present in all the phases. In BaTiO₃, except the lowest rhombohedral phase, the dipole moment formed by the B atom resonates between equivalent minima, and its possible observation depends on the “frequency scale” of the experimental method (see below).

2. The $d^0 - d^{10}$ problem and origin of multiferroicity is one of the up-to-date issues widely discussed in the literature. The first question is why, in the variety of transition metal perovskites ABO₃, for a long time only those with the transition metal B atom that has the $d^0$ configuration were considered as possible ferroelectrics (the “$d^0$ mystery" [16]), and only recently a limited number of some other systems with $n>0$ were shown to exhibit ferroelectric properties. For instance, why is BaTiO₃ ferroelectric, whereas BaVO₃ with the nearest neighbor transition metal V that has the $d^1$ configuration is not ferroelectric [37]. This feature is important in search for ferroelectric magnets (multiferroics) because only $d^n$ perovskites with $n>0$ may have unpaired electrons with nonzero magnetic moments. The vibronic theory elucidates directly this problem as shown in Section 3. Table 2 summarizes these conditions; it explains the origin of the observed ferroelectricity in a variety of perovskites [16, 17], for instance in CaMnO₃ [38] and LaCrO₃ [39]. The vibronic theory directly explains also why the ferroelectricity in CaMnO₃ increases with negative pressure and by substitution of Ca with Ba: it increases the volume of the unit cell and the Mn—O distance decreasing the rigidity $K_0$ in the condition of instability $\Delta<4F^K/K_0$ (see below). In addition to formulating the necessary conditions of multiferroicity the PJTE predicts the phenomenon of magnetic-ferroelectric crossover with a variety of magnetoelectric effects.

3. Direct Dependence on chemical composition. As in the examples above, the PJTE is very sensitive to the chemical composition of the system. In addition to the considered in more detail dependence of the ferroelectric and multiferroics properties on the $d^n$ configuration of the B ion in the ABO₃ perovskites, the dependence of these properties on the kind of transition metal with this configuration, namely $3d^n$, $4d^n$, $5d^n$, ..., as well as on the A ion can also be elucidated qualitatively in the vibronic theory. First, similar to the negative pressure mentioned above, the size of the A atom in ABO₃ determines the B—O distance (Fig. 2) and the strength of its inner $\sigma$ bonds that contribute to the $K_0$ value: with increase of the B—O distance the $K_0$ value decreases.
(and the derivative in the expression for \( F \) in Eq. (11) increases) facilitating the condition of instability \( \Delta < 4F^2/K_0 \). This explains why, in the series of \( 3d^0 \) titanates \( \text{CaTiO}_3, \text{SrTiO}_3, \text{BaTiO}_3 \) with increasing size of the A atom from left to right, only \( \text{BaTiO}_3 \) is ferroelectric, \( \text{SrTiO}_3 \) being a virtual ferroelectric, and \( \text{CaTiO}_3 \) is non-ferroelectric. Approximate numerical calculations confirm this conclusion [40]. This effect is also observed in \( \text{CaMnO}_3 \) crystal [38] where the substitution of Ca with Ba increases significantly its ferroelectric properties. For the same reason the crystal \( \text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3 \) becomes ferroelectric only at \( x \geq 0.45 \) [41]. For a similar reason only \( \text{BaTiO}_3 \) is ferroelectric in the series \( \text{BaTiO}_3, \text{BaZrO}_3, \text{BaHfO}_3 \); the B—O bonding distance in this series decreases (and hence \( K_0 \) increases) from left to right because of the increase of the size of the B atom in the approximately fixed positions of the oxygens that is controlled by the size of the A atom (Ba). As mentioned above, we assume here that the A ion is “inactive” in the sense that it does not produce a strong PJTE with distortions, but there may be cases when this ion is the center of the trigger mechanism of ferroelectric distortions instead of (or in combination with) the B ion. Note also that the multiferroic properties depend also on B ion environment that produces either low-spin or high-spin configurations [18].

4. Disorder and dynamics in the higher-temperature phases and the order-disorder nature of the phase transitions. The experiments on X-ray diffuse scattering show that only the lowest-temperature phase in \( \text{BaTiO}_3 \) and \( \text{KNbO}_3 \) are fully ordered, whereas the higher-temperature phases are partially disordered and the paraelectric phase is fully disordered. This picture was predicted qualitatively in the first paper on the vibronic theory in 1966 [10]. Further confirmation of this phenomenon was obtained in the EPR experiments with probing ions [27, 28], in NMR measurements [33, 34], etc. In the EPR experiments the \( \text{Mn}^{4+} \) ions that substitute \( \text{Ti}^{4+} \) ions was shown to follow the \( \text{Ti}^{4+} \) positions (according to Table 2 this ion in perovskites is “ferroelectric”); in the rhombohedral phase the Mn ion is shifted off-center to the trigonal [111] minimum of the APES, as expected, but at the phase transition to the orthorhombic phase the EPR signal broadens and disappears, while relaxation measurements show that in this phase the ion performs hoping between two near-neighbor equivalent but differently oriented minima with a characteristic correlation time of the reorientational hoping \( \tau \sim 10^9-10^{10} \) s. No displacive theories can explain these experimental observations that follow directly from the vibronic theory.
5. Relativity to the means of observation due to the dynamics of the ferroelectric ion. This is yet another feature of the ferroelectrics under consideration that has nothing to do with displacive theories and get full explanation in the vibronic theory. Because of the dynamics of the ferroelectric ions there may be differences in experimental observations of the same phenomena with different methods. This effect can be attributed to the essential different time-scales of these methods, different “time of measurement” $\tau'$ in comparison with the time $\tau$ of the reorientational hoping of the metal ion between the minima of the APES, as well as to different space-scale measurements as compared with the unit cell dimensions [28, 31, 33].

With regard to the time-scale, the conclusions from the experimental data may be different for experiments with $\tau'>\tau$ and $\tau'<\tau$ because of the full or partial averages over the reorientation positions (APES minima) observed in the former case. In particular, the origin of apparent differences in the interpretation of the experiments on NMR [33] and XAFS [31] at the tetragonal–paraelectric phase transition in BaTiO$_3$ were explained as due to the essential difference in the time-scales of the two methods of measurement [31]: in NMR $\tau'\sim 10^{-8}$ s which is larger than $\tau\sim 10^{-9}$-10$^{-10}$ s [14, 15] whereas in XAFS $\tau''\sim 10^{-15}$ s, which is smaller than $\tau$.

As for the partial displacive contribution to the phase transition which is seen in some of the experiments, it can be attributed to the space averages. Indeed, for instance, in the tetragonal phase, according to the vibronic theory described above, the system resonates between four minima situated along one of the tetragonal axes, so as in average the unit cell is tetragonally distorted. Since in the tetragonal phase the lattice is ordered in this tetragonal direction, the crystal is tetragonally distorted too. This is seen as a displacive component in the paraelectric-tetragonal phase transition in experiments that perceive the averaged picture [28, 36]. For transitions between the tetragonal to orthorhombic and the latter to rhombohedral phases such effects are expected to be less pronounced because they are accompanied by changes in dynamics of only two minima. Note that the wavelength in the usually employed optical measurements of soft modes is much larger than the unit cell where the dynamics of the ions at the order-disorder phase transition takes place; the observed picture in such measurements is averaged over many unit cells, thus seen as a displacive component.

6. Anharmonicity, orbital hybridization, and unusual atomic charges. In some approaches to the theory of ferroelectricity it is assumed that the ferroelectric properties occur due to significant lattice anharmonicity; the eight-minimum APES that emerges from PJTE theory is also a kind of
anharmonicity. In particular, in the theory of ferroelectricity (see, e.g., [42]) the main
interaction potential between the ions is taken expanded in series including anharmonic terms up
to fourth order. Meanwhile, there is a rigorously proven theorem showing that potentials
expanded in series up to the fourth order do not produce the eight-minimum surface [43]. This
means that the proper (lattice) anharmonicity that emerges from the higher order terms in the
Hamiltonian may be insufficient to reproduce the phenomenon. In addition, the lattice
anharmonicity is expected to be approximately the same in related perovskites, and it is not clear
why this anharmonicity is so specific and so strongly dependent on the chemical composition
and electronic structure in ferroelectrics.

This situation is fully clarified in the vibronic theory. Indeed, it is known that the PJTE, by
mixing electronic states under nuclear displacements produces a special additional anharmonicity
which may be much stronger than the lattice one (vibronic anharmonicity [2, 3]). The vibronic
anharmonicity is strongly related to the atomic and electronic structure of the crystal and may
produce rather sophisticated APES (see Eq. (14)) thus explaining directly the dependence of the
ferroelectricity on the composition of the crystal. The PJTE is not equivalent to proper (lattice)
anharmonicity, it takes place without the anharmonicity terms in the Hamiltonian, and this is one
of the important features of the vibronic theory.

Another important feature of ferroelectricity that emerges from some theoretical calculations
is the hybridization of the B metal $d$ orbitals with the $2p$ orbitals of the oxygen atoms due to the
ferroelectric distortion. This true observation follows directly from the PJTE for which the
orbital mixing producing added covalence is the driving force. With regard to unusual atomic
charges that some authors assume to explain ferroelectric properties (see in [13] ), there is neither
(based on first principles) theoretical, nor experimental evidence of their feasibility. On the
contrary, such charges contradict to the existing experience of electronic structure calculations,
and they are hardly possible from a thermodynamic point of view.

5. Conclusions

One of the main goals of this paper is to affirm that as a PJTE ferroelectric symmetry
breaking in perovskite lattices is of local origin, and to reverse the long-standing understanding
of the origin of ferroelectricity in ionic crystals as due to the compensation of the local repulsion between the ions by the long-range dipole-dipole interactions, by showing that under certain conditions the local dipolar distortions occur due to the PJTE independent of the long-range interaction, and the ferroelectric phase transitions in these cases are not displacive, but of order-disorder type.

This basic idea was first formulated in 1966, and to present day got full experimental confirmation. It emerges directly from the theorem of instability which proves that the ferroelectric sublattice displacements are triggered by the local dipolar instability induced by the PJTE; dependent on the parameter values, the latter can be either enhanced or damped by the long-range interactions. DFT calculations for the BaTiO₃ crystal as a whole and its several clusters confirm that the local off-center displacements of the Ti ion are not induced by long-range interactions. The vibronic PJTE coupling between the ground state (formed mainly by oxygen orbitals) and excited states (mainly Ti ion orbitals) produces a local eight-minimum APES with two kinds of saddle points, confirmed independently by the DFT calculations. The theory solves also the $d^{9}-d^{10}$ problem, showing directly how and why proper ferroelectric and multiferroic properties may depend on the number of $d$ electrons and their spin arrangement. In combination with the spin-crossover phenomenon a novel effect of magnetic-ferroelectric crossover is predicted. For BaTiO₃ the parameters of the theory are in reasonable agreement with the experimental data.

Most important are also the general qualitative aspects of the theory which explain the major properties of perovskite ABO₃ ferroelectrics and multiferroics that cannot be understood in the usual displacive theories. These include the trigonal off-center displacement of the B atom in the paraelectric and ferroelectric tetragonal phases, the characteristic dependence of the properties on the chemical composition (A and B ions) and the $d^6$ electronic configuration of the B atom, the origin of the observed B atom dynamics in the higher-temperature phases and order-disorder phase transition, and the role of anharmonicity and orbital hybridization. Of special interest is also the predicted by the theory dependence of the experimental observations on the method of measurement which is due to the local (tunneling or hoping) dynamics of the ferroelectric ion B, and the relation of the time scale of the method of measurement to this dynamics. For this reason, for instance, EPR, NMR, and XAFS measurements show different results. Because of the local character of the ion dynamics, the experimental measurements depend also on the wavelength of
the employed irradiation; as this wavelength usually covers many unit cells, the outcome of the experiment is seen as an averaged “displaceive” component (which is in fact not there).

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