Pseudo Jahn-Teller effect in permittivity of ferroelectric perovskites

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Abstract. Microscopic origin of dielectric susceptibility and permittivity of cubic ferroelectric perovskites $ABO_3$ (BaTiO$_3$, KNbO$_3$, etc.) in their high-symmetry paraelectric phase is explored. Ferroelectricity in these crystals is due to the strong pseudo Jahn-Teller effect (PJTE) resulting in off-centre instability of the transition metal ion B. In addition to the noticed earlier big enhancement of the permittivity by the local PJTE, it is found that the latter induces also anisotropy, contrary to widespread expectation for isotropic polarization in cubic crystals. The temperature and field dependence of polarization, dielectric susceptibility, and permittivity, as well as their angular dependence, are revealed as resulting from the local PJTE instability by numerical diagonalization of the Hamiltonian including the vibronic coupling and temperature-averaged interaction with the external electric field.

1. Introduction

We consider the dielectric susceptibility and permittivity of ferroelectric perovskites $ABO_3$, like BaTiO$_3$, KNbO$_3$, etc., in which the polar instability of the elementary-cell octahedron $[BO_6]$ is due to the pseudo Jahn-Teller effect (PJTE) [1-3]. The adiabatic potential energy surface (APES) of this octahedron was shown to have eight equivalent wells situated along the four trigonal axes $C_3$ (figure 1), in which the atom B is off-center shifted making a local dipole moment, with potential barriers between the wells. At higher temperatures, in the paraelectric phase the local polar displacements in different centers have arbitrary (incoherent and dynamic) orientations that make the macroscopically averaged crystal seen as cubic. At a lower temperature $T = T_C$, the ferroelectric phase transition results in orientation ordering of the local dipoles (partial or full) resulting in a polarized crystal, and the multi-valley APES explains the temperature-dependent formation of all the four ferroelectric phases [1].

A detailed presentation of this vibronic coupling theory is given in a series of papers [1, 2] and books [3] including a recent more elaborate theoretical description based on the Green’s functions approach [1]. Its main conclusions are confirmed in dozens of experimental observations forming a pattern (see one of them in [4] and many others cited in [1-3]). Recently the theory was expanded to also include the possibility of coexisting PJTE-induced ferroelectric and open-shell magnetic properties in perovskites $ABO_3$, and a table was given listing the B atoms with electron configurations...
that can produce such a multiferroic [2]. A possibility of magnetic-ferroelectric crossover is predicted there as well.

For BaTiO$_3$ in the paraelectric phase numeric estimates [5] show that the energy barrier between the minima of the APES is rather low, of the order of 200 cm$^{-1}$, but the vibrational frequency in the direction to the barrier is also low, so the zero-vibrations level is at about half the barrier height, at ~100 cm$^{-1}$. Hence we may expect the tunneling transitions between the minima at low temperatures being overwhelming with more intensive over-the-barrier transitions at higher temperatures. Accordingly is moving the vector of the dipole moment formed by the Ti$^{4+}$ ion positioned in the minima. For an ensemble of dipolar molecules oriented by an external electric field and disoriented by thermal motions the dielectric constant $\varepsilon$ was estimated by Debye [6]. It includes two contributions. One is the displacive term. It takes into account the polar distortion (polarization) of the molecule by the external electric field. The other one, the orientation contribution, comes from the orientation of the dipole moment by the field. The classical Debye-Curie-Weis-Langevin theory takes into account both these contributions to permittivity $\varepsilon$, as well as its dependence on the electric-field frequency $\omega$:

$$\varepsilon(\omega) = \varepsilon_0 \left( 1 + \frac{\chi_d}{1 + \omega^2 \tau_d^2} + \frac{\chi_o}{1 + \omega^2 \tau_o^2} \right)$$

(1)

Here $\varepsilon_0$ is the electric constant (also known as the permittivity of the vacuum), $\chi_d$ and $\chi_o$ are the electric susceptibilities of displacive and orientation contributions, respectively, and $\tau_d$ and $\tau_o$ are the corresponding relaxation times.

Usually the displacive contribution $\chi_d$ is relatively small; in molecular systems and ionic crystals in static electric fields ($\omega = 0$) it varies within the limits $\chi_d \sim 0.1 \div 10$. The orientation contribution $\chi_o$ for systems with a proper dipole moment is much larger (for water $\chi_d = 5$, $\chi_o = 75$), but there is no orientation effect in nonpolar molecules and in crystals without the JTE or PJTE. In BaTiO$_3$ the permittivity in the paraelectric phase reaches the value of $\varepsilon/\varepsilon_0 \approx 20,000$, and as was recently shown [7], in estimates by orders of magnitude that almost all of it comes from the orientation contribution of the PJTE-induced rotating dipole moments in the Ti centers. Without the PJTE, there is no other explanation of this giant permittivity and a similar strongly enhanced flexoelectricity [7].

Note that for these giant effects to take place in matter, the only requirement is the presence of local centers with polar instability in several (or infinite number of) equivalent directions with free or hindered rotations of the dipoles (the case of free rotation of the dipoles is similar to a polar liquid). In the perovskites ABO$_3$ under consideration such polar centers may occur at B sites (in the clusters [BO$_6$]) due to the PJTE. In the most studied case of BaTiO$_3$ the polar instability is strong with an eight-minimum APES, but relatively shallow barriers between the wells. Therefore, the rotation of the
local dipoles (either by tunneling or by over-the barrier transitions) is hindered. In other perovskites such a possibility may occur subject to the local ground state being sufficiently close in energy to excited electronic states (bands) with the same spin multiplicity but opposite parity [1–3]. Similar conditions apply to any other atomic centers in matter. In all these cases free or hindered rotation of the dipoles may occur causing an enhanced response to external perturbations. The free rotation case comes about when, instead of the considered in this paper multi-minimum case, the JTE or PJTE results in a two-dimensional trough.

In anisotropic crystals the linear polarization \( \mathbf{P} \) by the electric field \( \mathbf{E} \) is a tensor, \( P_j = \Sigma \delta_{jk} E_k \). Accordingly, the permittivity is a symmetric tensor of the second rank, \( \varepsilon_{jk} = \varepsilon_0 (1 + \chi_{jk}) \). In cubic crystals the main three components of the tensor \( \varepsilon_{jk} \) coincide, and the permittivity is isotropic. On the other hand, in ferroelectric crystals with PJTE the orientation contribution to the susceptibility \( \chi_0 \) should depend on the direction of the electric field. Indeed, as mentioned above, each elementary cell of such a crystal is unstable with respect to the displacement of the central atom along trigonal axes \( C_3 \), hence the magnitude of the vector \( \mathbf{P} \) is a maximum when the electric field vector \( \mathbf{E} \) points along one of these axes. It follows that in these ferroelectric crystals the permittivity should have a cubic anisotropy, even in the cubic paraelectric phase where it is expected to be isotropic in the absence of the PJTE.

In the present paper we report temperature and field dependence of the polarization, dielectric susceptibility, and permittivity, as well as their anisotropy in cubic-perovskite ferroelectrics of the type \( \mathrm{ABO}_3 \), subject to the PJTE in the B centers. In the alternating external electric field the frequency dependence \( \varepsilon(\omega) \) includes the contribution of both the electrons and nuclei, but the contribution of the latter to \( \varepsilon(\infty) \), due to their inertia, is negligible. Considering here the anisotropy of \( \chi \) and \( \varepsilon \) due to nuclear displacements, we limit our analysis to the case of static electric field, meaning \( \omega = 0 \). The frequency dependence \( \varepsilon(\omega) \) is shown in equation (1). In the paraelectric phase there is no spontaneous polarization, hence interaction between the active PJTE centers is not significantly strong. Therefore we ignore the cooperative effects and, with respect to the local PJTE properties we consider each elementary cell independently.

Specifics of the calculation presented in this paper relate to the most studied case of \( \text{BaTiO}_3 \). However, derived here qualitative conclusions apply to all ferroelectric perovskites \( \text{ABO}_3 \) as long as the PJTE is strong enough to provide instability of the on-center position of the atom B in the cubic phase. This is due to the overall cubic symmetry of the eight-minimum APES. Details, similarities, differences, and possible implications of the PJTE in other cubic perovskites in the variety of transition metal ions from \( d^0 \) to \( d^{10} \) are discussed in [2].

In the next section 2 we introduce the vibronic Hamiltonian of the octahedral cluster \( [\text{BO}_6] \) of each elementary cell of the cubic-perovskite crystal, the eight-minimum APES induced by the PJTE, and the reduction of the Hamiltonian to the \( 8 \times 8 \) matrix in the space of the \( 8 \) vibronic basis states localized in the eight trigonal minima. Section 3 shows the main results obtained by numerical calculations, while the conclusions in section 4 are devoted to some further discussion of the results.

2. PJTE origin of the polar instability of the elementary octahedron \( [\text{BO}_6] \). The eight-minimum model

2.1. Background

The origin of ferroelectric instability in cubic-perovskite \( \text{BaTiO}_3 \) as due to the local off-centre displacements of the Ti\(^{4+}\) ion in the octahedron \([\text{TiO}_6]\) induced by the PJTE was first introduced in 1966 [1]. In molecular orbital (MO) presentation the polar instability of this octahedron is due to the vibronic coupling between the highest occupied MO (HOMO), which are mostly oxygen 2p-orbitals, with the lowest unoccupied MO (LUMO) which are mostly \( \ell_{2g} \)-type 3d-orbitals of the Ti\(^{4+}\) (figure 2). In the absence of external perturbations and internal random fields the vibronic Hamiltonian of the octahedron \([\text{TiO}_6]\) can be presented in the matrix form as follows:
\[ H_0 = \Delta C_0 + \frac{1}{2m^*} \left( p_x^2 + p_y^2 + p_z^2 \right) + \frac{1}{2} K_0 \left( q_x^2 + q_y^2 + q_z^2 \right) + H_{\text{PJTE}} \]  

where \( p_a \ (a = x, y, z) \) are the components of the linear momentum \( p \) conjugated with the coordinates \( q_a \ (a = x, y, z) \), the components of the vector \( q \) transforming as \( T_{1u} \), \( K_0 \) is the primary force constant, and \( m^* \) is the effective mass. The motion of the center of mass of the octahedron [TiO\(_6\)] is separated out, so \( q \) includes off-center displacements of the ion Ti\(^{4+}\) and the opposite motion of the oxygen octahedron \( O_a \). The 9 \times 9-matrix \( C_9 \) is the electronic part of the Hamiltonian presented in the basis of the nine one-electron states (figure 2) mixed by the three polar modes \( q_a \ (a = x, y, z) \) active in the PJTE. The parameter \( 2\Delta \) is the HOMO-LUMO energy gap and \( H_{\text{PJTE}} \) stands for the Hamiltonian of the PJTE vibronic coupling of the nine electronic states (HOMO and LUMO) to the three modes \( q_a \). In the linear approximation we can set \( H_{\text{PJTE}} = F(C_{\alpha}q_{\alpha} + C_{\beta}q_{\beta} + C_{\gamma}q_{\gamma}) \) where \( F \) is the linear vibronic coupling constant and \( C_{\alpha}, C_{\beta}, \) and \( C_{\gamma} \) are matrices \( 9 \times 9 \) acting in the basis of the nine HOMO-LUMO states. They are composed of the corresponding Clebsch-Gordan coefficients taken from [8]. In these matrices the coefficient \( 1/\sqrt{2} \) is factored out and included in the vibronic constant \( F \). The explicit form of the matrices \( C_{\alpha}, C_{\beta}, C_{\gamma} \) as well as the details of the solution of the corresponding PJTE problem are given in [1].

Figure 2. MO energy level diagram for the octahedral cluster [TiO\(_6\)]\(^{8-}\) (after [1]). Shown in red are energy levels of the nine HOMO-LUMO states \( t_{1u}, t_{2u}, \) and \( t_{2g} \) coupled to the odd-parity modes \( q_x, q_y, \) and \( q_z \) active in the PJTE. \( 2\Delta \) is the energy gap between LUMO and HOMO.

A more elaborate treatment of the problem going beyond the cluster model was given recently by means of the Green’s function’s approach [5]. It allowed taking into account the interaction of the B center with the whole crystal via the electronic and vibrational band structures. The Hamiltonian (2) was shown to be the effective Hamiltonian if the parameters \( K_0 \) and \( \Delta \) are substituted by their weighted averages over the electronic and vibrational bands.

Note that the vibronic coupling makes the electronic states dependent on the nuclear coordinates \( q = \{q_x, q_y, q_z\} \). It takes place in the first order of perturbation theory with respect to \( H_{\text{PJTE}} \). For instance, one of the HOMO, the \( t_{1u}(z) \), formed mostly from the oxygen orbitals \( 2p \), under the \( t_{1u} \) nuclear displacements acquires an admixture of the orbital \( t_{2g}(yz) \), one of the three LUMO, the \( t_{2g} \) orbitals of the central atom B:

\[
\psi(r, q) = \psi_{t_{1u}}^{(z)}(r, 0) + F \sum_{a=x,y,z} \frac{\langle \psi_{t_{1u}}^{(z)}(r, 0) | C_a | \psi_{t_{2g}}^{(yz)}(r, 0) \rangle}{E_{t_{1u}} - E_{t_{2g}}} q_a \psi_{t_{2g}}^{(yz)}(r, 0) 
\]  

were \( r \) is the electronic coordinate. Two important conclusions (often missed in publications) follow from this, at first sight simple expression:

(a) in the absence of the PJTE, when \( F = 0 \), the last term in equation (3) is zero and the wavefunction of the \( t_{1u}(z) \) HOMO under consideration remains “frozen” atomic, \( \psi_{t_{1u}}(r, 0) \), in spite of nuclear displacements. It follows that without the PJTE the HOMO orbitals are “bound” to the symmetrical positions of the nuclei and do not follow their displacements in the first order. In the last
term in equation (3), the matrix elements in the numerator describe the emergent nonzero overlap of HOMO with LUMO which are orthogonal in the regular octahedron. Due to the PJTE symmetry breaking (figure 3) the symmetry restriction is lifted and the overlap becomes not equal to zero. Added overlap means added covalence bonding between the reference atoms. It becomes possible only due to the contribution of the \( \mathbf{H}_{\text{PT}} \), i.e. the PJTE. This conclusion is a part of the general statement that the only source of symmetry breaking in polyatomic systems is the PJTE in nondegenerate states and the JTE in degenerate states (see in [1-3]).

(b) The second term in equation (3) is proportional to the ratio \( F/(2\Delta) \), where \( 2\Delta \) is the noted above HOMO-LUMO energy gap (figure 2). The larger \( F/(2\Delta) \), the stronger the added covalency and the PJTE, provided the stiffness of the system \( K_0 \) is the same. For a long time smallness of the energy gap \( 2\Delta \) was believed to be the primary criterion of the efficiency of the PJTE. However, as was shown by numeric calculations [9], the PJTE instability may take place even if this gap is very large (~14 eV in the planar configuration of \( \text{NH}_3 \)), provided the other two parameters in its criterion, \( K_0 < F^2/(2\Delta) \) (introduced in [6], the first paper on this effect) are appropriately significant. In \( \text{BaTiO}_3 \) the energy gap \( 2\Delta \) is of the order of the band gap, \( 2\Delta \approx 2.5 \) eV. Actually, in the PJTE coupling to higher energy levels of the conduction band contribute as well, so the effective energy gap is larger. By numeric estimates of the relevant parameter values [5], it was shown that the condition \( K_0 < F^2/(2\Delta) \) is true and, therefore, despite the relatively large energy gap the polar instability in this crystal is due to the PJTE.

\[ \text{Figure 3. Illustration to the added covalency by the PJTE in the octahedron [BO}_6] \text{ shown in the } \text{yz} \text{ cross-section plane (after [5])}. \text{ The numbering of the atoms follows figure 1 with the oxygen atoms in blue and the B atom red. (a) The B atom is in the center of the octahedron. The HOMO } t_{1u}(z) \text{ is composed of oxygen orbitals } 2p_z. \text{ The LUMO is the orbital } t_{2g}(yz) \text{ of the central ion B. As the positive contributions are cancelled by the negative ones, the total overlap (shown in yellow) is zero; the LUMOs are orthogonal to HOMOs. (b) The off-center displacement of the B ion lifts the orthogonality of the HOMO-LUMO orbitals. The nonzero overlap induces additional covalency that facilitates the polar distortion.} \]

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2.2. APES of the cluster [BO\(_3\)] in perovskite crystals ABO\(_3\)

In search for the adiabatic potential energy we can ignore the kinetic energy term in equation (2). Diagonalization of the one-electron matrix Hamiltonian \( \Delta C_0 + \mathbf{H}_{\text{PT}} \) gives nine adiabatic eigenvalues \( \lambda_j(q_1, q_2, q_3) \) with \( j = 1, 2, ..., 9 \). In case when the central atom B is a transition metal ion with a \( d^0 \) shell, the lowest six ones correspond to HOMOs and the remaining three are LUMOs. Populating the HOMOs with 12 electrons (by 2 from each oxygen atom) we find the ground-state singlet adiabatic electron term [1], \( U(q_1, q_2, q_3) = \frac{1}{2} K_0 q_3^2 - 2 \sqrt{\Delta^2 + 2F^2(q_3^2 - q_0^2)} - 2 \sqrt{\Delta^2 + 2F^2(q_0^2 - q_3^2)} - 2 \sqrt{\Delta^2 + 2F^2(q_0^2 - q_3^2)} \) with \( q_0 = q_1 = q_2 = q_3^2 \). Its extremes were analyzed in the first paper on this subject [1]. Under condition of a relatively strong PJTE, \( 8F^2/\Delta > K_0 \), the ground-state APES \( U(q_1, q_2, q_3) \) was shown to have a maximum at the center, \( q = 0 \), and, also, eight symmetry-equivalent minimum points
where the atom B is off-center shifted along trigonal symmetry axes as shown in figure 1. The trigonal wells are separated by six tetragonal and 12 orthorhombic saddle points.

The overall landscape of the surface $U(q_x, q_y, q_z)$ is shown in figure 4. The eight equivalent wells correspond to the central atom off-center shifted along one of the four trigonal axes (see also figure 1). The coordinates of the trigonal minimum points are $(\pm Q_0, \pm Q_0, \pm Q_0)$, where $Q_0 = \frac{1}{2} \sqrt{(F/K_0) \sqrt{(64 - \delta^2)}}$, and $\delta = \Delta K_0/F^2$ is the dimensionless energy gap $\Delta$ in units of $F/K_0$. The nuclear energy at these points is $U(\pm Q_0, \pm Q_0, \pm Q_0) = -0.375(F^2/K_0) (64 + 16\delta + \delta^2)$. Next, higher in energy are the mentioned above orthorhombic saddle points shown in figure 4 by open circles, and six tetragonal saddle-points along the three coordinate axes (not shown in the figure) that are higher than the orthorhombic points.

![Figure 4. (a) APES of the cluster [BO₄] in 3D-space of the coordinates $q_x$, $q_y$ and $q_z$ (after [1]). Bold black dots indicate trigonal minima, while open circles are the orthorhombic saddle points. Red curves are trajectories of either tunneling or over-the-barrier transitions along the fastest steep-slope. (b) Tunneling splitting of the ground vibronic energy level](image)

The coordinates and energies are given in [1, 2, 5]. With the position, symmetry, and energy of the extremes of the APES we can estimate the sequence of order-disorder phase transitions by stepwise overcoming the corresponding barriers between the wells with temperature [1-3]. It explains the origin of all four phases in these crystals as following from the described above shape of the APES induced by the PJTE.

For the temperature of the paraelectric to ferroelectric phase transition in BaTiO₃ the estimate of the parameters of the APES yields [5]: $F \approx 4.7$ eV/Å, $K_0 \approx 97$ eV/Å², $\delta \approx 6.2$. For these parameter values trigonal wells are rather deep, $-0.2$ eV, but the lowest potential barrier between them is much smaller, $U[110] - U[111] \approx 200$ cm⁻¹. Similar values are obtained by DFT [5]. With the local vibrational frequency $\omega \sim 200$ cm⁻¹ we get the zero vibrational level at about 100 cm⁻¹, meaning that the transitions between the wells can take place via tunnelling at low temperatures and by over-the-barrier activation at higher temperatures. The tetragonal barriers along [100], [010], etc., are at about 560 cm⁻¹, meaning 2.75 higher than the orthorhombic barriers at 200 cm⁻¹. Therefore, practically the probability of direct tunnelling through them is zero. Over-the-barrier activation in this case becomes competitive at $kT > 800$K. At any reasonable temperature transitions via the regular cubic configuration at $q = 0$ with the barrier height of about 0.2 eV is impossible. It follows that in these systems tunnelling and over-the-barrier transitions between trigonal wells take place only via the orthorhombic saddle-points between them (shown in figure 4a in red lines).

2.3. Tunneling in the eight-minimum model

The model of an adiabatic potential energy surface with eight wells, irrelevant to their origin, was considered in [11], where it was assumed that, starting from a regular cube formed by the eight equivalent wells (see the cube $a$, $b$, $c$, etc., in figure 1), there are three types of tunneling transitions between any two of them: along the edges, the large diagonal, and the small diagonal. Accordingly, in the basis of the eight vibrational states localized in the eight wells, the corresponding overlap integrals...
$S_n = \langle k \mid n \rangle$ and matrix elements of the Hamiltonian $H_n = \langle k \mid H \mid n \rangle$ can be reduced to three types, respectively: $S, S'$, and $S''$, and $H, H'$, and $H''$. The eight basis functions form a reducible representation of the cubic group that splits into four irreducible representations: $A_{1g} + T_{1u} + T_{2g} + A_{2u}$. The symmetry adapted wave functions, which are the linear combinations of the states localized in the wells, and the corresponding eigenvalues are given in [11]. For the transitions along the edge, long diagonal, and short diagonal of the cube, the parameters of tunneling splitting are $\Gamma, \Gamma''$ and $\Gamma''$, respectively. 

As mentioned above, the only tunnelling and over-the barrier transitions to be included are via the orthorhombic saddle points. This means $\Gamma' = \Gamma'' = 0$, $H' = H'' = 0$, and $S = S'' = 0$. This assumption results in an equidistant tunneling energy level spectrum (figure 4b) with $E(A_{1g}) \approx E_0 - 3\Gamma$, $E(T_{1u}) \approx E_0 - \Gamma$, $E(T_{2g}) \approx E_0 + \Gamma$ and $E(A_{2u}) \approx E_0 + 3\Gamma$. For the sake of convenience, assume the ground state energy $E_0 = 0$. Then we get: $E(A_{1g}) \approx - 3\Gamma$, $E(T_{1u}) \approx - \Gamma$, $E(T_{2g}) \approx \Gamma$ and $E(A_{2u}) \approx 3\Gamma$.

3. The effect of external electric field

3.1 The dipole moment of the cluster [BO₆] and polarization of the crystal in external electric fields. In the trigonal wells of the APES the cluster [BO₆] has a dipole moment $\mathbf{d}$. In the electric field $\mathbf{E}$ the energy of the cluster is $- \mathbf{E} \cdot \mathbf{d}$. In general, $\mathbf{d}$ includes nuclear and electronic contributions, $\mathbf{d} = \mathbf{d}_{\text{nuc}} + \mathbf{d}_{\text{el}}$. To estimate the nuclear contribution $\mathbf{d}_{\text{nuc}}$, we present the coordinate $\mathbf{q}$ as a linear combination of the nuclear displacements $\mathbf{R}_k$ of each atom, $\mathbf{q} = \Sigma c_k \mathbf{R}_k$. We assume that the oxygen octahedron is of the mass $6m$, where $m = 16$ u is the mass of the oxygen atom, carries a charge of $6(2e) = -12e$, and moves as a whole with respect to the atom B without distortion (in fact, there is a small distortion of the oxygen’s octahedral configuration which we ignore). In this case the center of mass of the octahedron $\mathbf{R}_0$ coincides with its geometric center. When this octahedron shifts to the point $\mathbf{R}$ and the ion $\mathbf{B}$ with the mass $M$ moves to the point $\mathbf{R}_0$, the center of mass of the cluster [BO₆] moves to the point $\mathbf{R}_{\text{cm}} = (6m\mathbf{R} + MR_0)/(6m + M)$. Keeping the latter unchanged, $\mathbf{R}_{\text{cm}} = 0$, we get $6m\mathbf{R} + MR_0 = 0$, or $\mathbf{R}_0 = -(6m/M)\mathbf{R}$. In particular, for [TiO₆] we have: $M = 48$ u = 3 m and, therefore, $\mathbf{R}_0 = -2\mathbf{R}$. This means the displacement of Ti is twice those of the oxygen atoms, and in the opposite direction, its relative displacement being $\mathbf{q} = \mathbf{R}_0 - \mathbf{R}$. If we assume, as above, that the charge on B equals $+4e$, then $\mathbf{d}_{\text{nuc}} = (+4e)\mathbf{R}_0 + (-12e)\mathbf{R} = (4\mathbf{R}_0 - 12\mathbf{R})e$. With $\mathbf{R}_0 = (2/3)\mathbf{q}$ and $\mathbf{R} = (-1/3)\mathbf{q}$ we have $\mathbf{d}_{\text{nuc}} = (20/3)e\mathbf{q}$.

The dipole moment of the electrons, $\mathbf{d}_{\text{el}} = -e\mathbf{r}$, is proportional to the mean value $\bar{r}$ of the electron coordinate $\mathbf{r}$. In the ground state of the undistorted cluster, when $\mathbf{q} = 0$, we have $\bar{r} = 0$. Evidently, we can assume that $\bar{r}$ grows with $\mathbf{q}$, and in the first approximation $\bar{r} = \text{const} \cdot q$. For the system in one of the minima, say, the one along [111], the main contribution to the dipole moment comes from the six HOMO. Ignoring the small contribution from the admixture of $t_{2g}$ orbitals of the atom B, we find that $\bar{r}$ is approximately equal to the displacement of the oxygen octahedron $\mathbf{R}_0$, $\bar{r} \approx \mathbf{R}_0$, and with $\mathbf{R} = (-1/3)\mathbf{q}$ we come to $\bar{r} \approx -\mathbf{q}/3$. Accordingly, $\mathbf{d}_{\text{el}} = -e\bar{r} \approx eq/3$, and the total dipole moment of the cluster $\mathbf{d} = \mathbf{d}_{\text{nuc}} + \mathbf{d}_{\text{el}} \approx (20/3)e\mathbf{q} + (1/3)e\mathbf{q} = 7e\mathbf{q}$. Note that the nuclear contribution in the PJTE-induced dipole moment is 20 times larger than the electronic one. So, in a good approximation the latter can be neglected.

In an external electric field $\mathbf{E}$ the cubic-perovskite dielectric crystal ABO₃ becomes polarized. Induced by the field, the vector of the corresponding polarization $\mathbf{P}$ is linearly dependent of the electric field; its components are $P_j = \Sigma \chi_{jk}E_k$, where $\chi_{jk}$ are elements of the tensor of dielectric susceptibility of the system. Along symmetry axes vectors $\mathbf{E}$ and $\mathbf{P}$ are parallel and $\chi = P/E$. According to equation (1), in static electric field ($\omega = 0$) the permittivity $\varepsilon$ is determined by both the displaceable $\chi_d$ and the orientation $\chi_o$ contribution. However, as shown in [7], the latter is overwhelmingly greater, $\chi_o \gg \chi_d$, and, therefore, $\chi = \chi_o + \chi_d \approx \chi_o$.

The polarization is the volume density of the average dipole moment induced by the electric field, $\mathbf{P} = (\langle \mathbf{d} \rangle a^2)$, where $a$ is the crystal lattice constant and $\langle \ldots \rangle$ means averaging over the quantum states of the system with their Boltzmann population factors at the given temperature $T$. 

\[ \langle d \rangle = \frac{1}{Z} \sum_n \langle n | e^{-H_{0}T} d | n \rangle = \frac{1}{Z} \sum_n e^{-E_{n}T} \langle n | d | n \rangle, \quad Z = \sum \langle n | e^{-H_{0}T} | n \rangle = \sum_n e^{-E_{n}T} \] (4)

Here \(|n\rangle\) are the wavefunctions, and \(E_{n}\) are the eigenvalues of Hamiltonian \(H = H_{0} - E \cdot d\). In the basis of the eight tunneling states the matrix of this Hamiltonian is as follows:

\[
H = \Gamma \begin{pmatrix}
A_{g} & -3 & -1 & 0 & 0 & 0 & 0 & 0 \\
T_{1a}x & 0 & 0 & 0 & 0 & 0 & 0 \\
T_{1a}y & \alpha A & \beta A & \gamma A & 0 & 0 & 0 & 0 \\
T_{1a}z & \gamma A & \alpha A & \beta A & 0 & 0 & 0 & 0 \\
T_{2g} \xi & 0 & 0 & \gamma A & 0 & 0 & 0 & 0 \\
T_{2g} \eta & 0 & 0 & 0 & 1 & 0 & \beta A & \alpha A \\
T_{2g} \zeta & 0 & 0 & 0 & 0 & 0 & \alpha A & \beta A \\
A_{2u} & 0 & 0 & 0 & 0 & 0 & 0 & \gamma A \\
\end{pmatrix} \] (5)

All the parameters in this matrix are given in units of \(\Gamma\) which is factored out of the matrix. On the diagonal are the obtained above energies of the eight tunneling levels. The parameter of the electric field is denoted by \(A = -E_{d}\) where \(d_{0} = 7eQ_{0}/\sqrt{3}\) is the dipole moment of the cluster \([BO_{6}]\) when nuclear motion is localized in one of the trigonal wells, \(E = |E|\) is the magnitude of the applied electric field, while \(\alpha, \beta, \) and \(\gamma\) are the direction cosines of the electric field [13],

\[
\alpha = \frac{E_{x}}{|E|} = \cos \theta \cos \varphi, \quad \beta = \frac{E_{y}}{|E|} = \cos \theta \sin \varphi, \quad \gamma = \frac{E_{z}}{|E|} = \sin \theta
\] (6)

The results of numerical diagonalization of the matrix (5) and consequent calculations of the field-dependent tunneling energy levels, lattice polarizations \(P\), dielectric susceptibility \(\chi\), and their angular and temperature dependence are shown in figures 5–7. The results of numerical calculations of the polarization of the crystal \(P = \langle d \rangle/a^{3}\) with the vector \(d\) after equation (4) are given in figure 6, where its dependence on both the magnitude and direction of the applied electric field \(E\), as well as on temperature are shown. \(P\) is shown in units of \(P_{m}/a^{3}\) which is the maximum value of \(P\) reached at saturation along the direction [111] of the vector \(E\), while the magnitude of the vector \(E\) is given in

**Figure 5.** The variation of tunneling energy levels \(E_{n}\) (in units of \(\Gamma\)) of the cluster \([BO_{6}]\) with the magnitude of the external electric field \(E\) in units of \(\Gamma/d_{0}\). (a) The electric field is applied in the [001] direction. Energy levels are labelled by the irreducible representations of the reduced symmetry \(C_{4v}\). (b) Electric field is applied in the [110] direction. The reduced symmetry is \(C_{2v}\). (c) Electric field is applied in the [111] direction. The reduced symmetry is \(C_{3v}\).
units of \( E_0 = \Gamma/d_0 \), where \( \Gamma \), as above, is the tunneling parameter (figure 4b). From these data it follows, first, that there is a strong dependence of the orientation part of polarization on magnitude of the electric field. It should not be there without the PJTE. The displacive polarization of the ionic lattice is by several orders of magnitude smaller. Also, all graphs in figure 6 show saturation of the polarization beginning from the value \( E \approx 2\Gamma/d_0 \). This means polarization of the crystal comes close to saturation when the energy of the dipole moments in the electric field reaches the order of magnitude of the tunneling splitting (or over-the-barrier transitions). At this point the dipoles become fully oriented along the applied electric field. This confirms the previous estimates of the orientation contribution to the magnitude of polarization given in [7].

Next, the differences in \( P \) values in the three directions, trigonal \( \mathbf{E} \parallel [111] \), tetragonal \( \mathbf{E} \parallel [100] \), and orthorhombic \( \mathbf{E} \parallel [110] \) in figure 6 show that there is a significant angular dependence of the polarization (not considered in [11]) which, again, should not be there in a cubic crystal in the absence of the PJTE. Induced by the latter, the polarization is maximal along the trigonal axes, where the absolute minima are positioned, while the smallest \( P \) value emerges along the highest tetragonal saddle-points of the APES. The temperature and field dependent angular diagrams of the polarization \( \mathbf{P} \) are shown in figure 7.

**Figure 6.** Variation of the polarization \( P \) (in units of \( d_0/\alpha^2 \)) of the cluster \([\text{BO}_6]\) with the external electric field \( \mathbf{E} \) (in units of \( \Gamma/d_0 \)) along the main symmetry axes \([111]\), \([100]\) and \([110]\) at three temperatures.

**Figure 7.** Angular dependence of the polarization \( \mathbf{P} \) in the cross-section plane \( q_x = q_y, \phi = \pi/4 \) (see figure 1) at different temperatures and electric field magnitude \( \mathbf{E} \). The magnitude of \( \mathbf{P} \) is maximal along trigonal directions, \( |q_x| = |q_y| = |q_z| \), lower in the orthorhombic, and minimal in the tetragonal directions.
A qualitative explanation of this orientation effect is illustrated in figure 8 in which the cross-section of the APES in the plane (110), \( q_x = q_y \), is shown (cf. figure 4a). In sufficiently weak fields \( E \ll \Gamma/d_0 \), all the trigonal minima remain approximately equivalent (see the left-hand side of figure 8). In a stronger field, for instance, when \( E \gg \Gamma/d_0 \) and \( E \parallel [111] \), energy of the trigonal minimum with the coordinates \((Q_o, Q_o, Q_o)\) is lowered, whereas the energy of the one at \((-Q_o, -Q_o, -Q_o)\) is elevated, and there are similar differences between the other minima, which manifest pairwise correlation along and opposite to the direction of the applied electric field. As a result the nuclear motion is ultimately localized in the lowest well, at which point the orientation contribution to the dielectric susceptibility \( \chi_0 \) is frozen, and only a small contribution of the displacive one is left.

The cubic anisotropy of the polarization is due to the different magnitude of the average dipole moment at different direction of the vector \( E \). For \( E \parallel [111] \) in saturation all the dipoles are frozen in the lowest trigonal well along the field with the dipole moment \( d_0 \) of the unit cell. In the case when \( E \parallel [110] \), two of the eight wells are lowest in energy. As they remain symmetry-equivalent in the field \( E \parallel [110] \), the resonance conditions for tunneling are kept. The tunneling between them results in an average dipole moment of \((\sqrt{2/3})d_0\). If the applied electric field points along the tetragonal axes, \( E \parallel [100] \), four wells remain equivalent in the field along the tetragonal axes, resulting in the average

\[
\frac{\chi}{\chi_{sc}} = \frac{d_0^2}{(3\Gamma\epsilon_0 a^3)}, \quad \text{where} \quad d_0 \text{ is the dipole moment of the unit cell with the B atom in the trigonal minimum and } \Gamma \text{ is the tunneling parameter, while } E \text{ is given in units } \Gamma/d_0.
\]
dipole moment equal to \((1/\sqrt{3})d_0\). The calculated values of \(P\) in figure 6 fully agree with these qualitative predictions.

3.2. Dielectric susceptibility and permittivity.

The variation of dielectric susceptibility \(\chi\) with the magnitude of the applied electric field pointing in three directions, \(E \parallel [100]\), \(E \parallel [110]\) and \(E \parallel [111]\), at three characteristic temperatures, is shown in figures 9 and 10. Diagrams of its angular dependence are qualitatively the same as for the polarization \(P\) in figure 7. The value of \(\chi\) is given in units of the dimensionless scaling parameter \(\chi_{sc} = d_0^2/(3\varepsilon_0\Gamma a^3)\) which is the ratio of the units for \(P\) in \(d_0/a^3\) and \(E\) in \(\Gamma/d_0\) (to compare, in BaTiO\(_3\) the magnitude of \(\chi_{sc}\) is about \(0.45\cdot10^3\) [7]). As the field dependence of \(P = f(E)\) is nonlinear, the susceptibility \(\chi\) is introduced as the derivative \(\chi = \varepsilon_0^{-1}(\partial P/\partial E)\) [14]. As expected, \(\chi\) goes to zero in sufficiently strong electric field. In a very strong electric field, at saturation, where \(P\) is constant, we have \(\chi = \varepsilon_0^{-1}(P/E)\). At this point only the displacive contribution to permittivity \(\varepsilon\) is left, whereas the difference in their angular dependence increases with the field (figure 7). These specific properties of permittivity follow directly from the eight-minima shape of the APES induced by the local PJTE and, as shown above in figure 8, the dynamics of localization of the nuclear motion in the lowest wells that are along the applied electric field.

![Figure 10](image.png)

**Figure 10.** Temperature dependence of the dielectric susceptibility \(\chi\) [in units of \(\chi_{sc} = d_0^2/(3\varepsilon_0\Gamma a^3)\)] of the cluster [BO\(_6\)] at three directions of the external electric field, \(E \parallel [111]\), \(E \parallel [100]\) and \(E \parallel [110]\), and three absolute values, \(E = 0.01\Gamma/d_0\), \(\Gamma/d_0\), and \(2\Gamma/d_0\). The temperature is given in dimensionless units \(kT/\Gamma\).

The angular dependence of the dielectric susceptibility can be modeled by the first terms in the expansion in cubic harmonics,

\[
\chi(E) \approx \chi_0(E) + \chi_4(E)Y_4(\theta, \varphi)
\]

where \(\chi_0\) is the isotropic contribution, \(\chi_4\) is the anisotropic amplitude, and \(Y_4(\theta, \varphi)\) is the fourth order cubic harmonic, \(Y_4(\theta, \varphi) = (x^4 + y^4 + z^4 - \frac{1}{2} r^4)/r^4\). By fitting the numerical values of the anisotropy in figure 9 for \(kT = \Gamma\) we find:

\[
\chi_0 \approx 0.89 - 0.43\frac{Ed}{\Gamma} + 0.058\left(\frac{Ed}{\Gamma}\right)^2, \quad \chi_4 \approx 0.017 - 0.39\frac{Ed}{\Gamma} + 0.102\left(\frac{Ed}{\Gamma}\right)^2
\]

where \(E = |E|, d = |d|, \) and \(\Gamma\) is the tunneling parameter, same as above.
The temperature dependence of $\chi$ is shown in figure 10. As expected, in accordance with equation (4), it drops with temperature approaching zero at $T \to \infty$. At high temperatures all the tunneling states are equally populated, the common factor $\exp\left(-E_s/kT\right)$ can be factored out in the equation (4), while the trace of the operator $d$ is zero.

4. Conclusion
In this paper ferroelectric cubic perovskites $\text{ABO}_3$ are considered. All approximations used above and most of the numeric results shown in figures 5 - 10 are based upon estimates made in [5] for barium titanate, the most studied member of the large class of cubic perovskites $\text{ABO}_3$. Similar to the case of $\text{BaTiO}_3$, the PJTE in the octahedral B centers results in an eight-minimum APES with a dipole moment in the wells. Although the actual magnitudes of the observable effects vary for different ferroelectric perovskite oxides, qualitatively they are expected to be similar to the ones reported above. The important condition for this similarity is polar off-center instability of the octahedral cluster $[\text{BO}_3]$. Resulting from the PJTE, it manifests itself in a strongly anharmonic APES of the ground-state electron term with a maximum at the on-center and a wrapped trough with alternating minimum and saddle-point off-center positions of the metal ion B. The local PJTE in octahedral clusters $[\text{BO}_3]$ creates local rotating dipoles. Such systems manifest a significant enhancement of permittivity of orientation origin unexpected without the PJTE.

This is a general feature of all ferroelectric perovskites $\text{ABO}_3$. It follows from their cubic crystal symmetry in the high-temperature paraelectric phase. If, distinguished from the $d$ case of $\text{BaTiO}_3$, for the central atom B there are several $d$ electrons present in the outer shell or, not 3$d$ but, say, 4$d$ orbitals (as in $\text{KNbO}_3$) are involved in vibronic coupling, still the PJTE is possible [2] provided the fraction $F^2/K_0$ is strong enough compared to the band gap $\Delta$. Depending on a particular $d^n$ configuration, the corresponding inequality relating $F^2/K_0$ to $\Delta$ includes a numeric factor (e.g., in the $d^3$ case the inequality is $8F^2/K_0 > \Delta$ with the factor of 8). However, for a ferroelectric perovskite $\text{ABO}_3$ under consideration, its ferroelectric feature with the polar instability of on-center position of the ion B is a direct indication that the corresponding inequality is true.

Also, the enhanced permittivity has unexpected angular dependence. Rotation of the dipoles is hindered by either tunneling or over-the-barrier transitions. The crystal is assumed to be in its paraelectric phase. Therefore, in the absence of external perturbations the rotational motion of the local dipoles is assumed to be uncorrelated (not ordered). Besides, depending on the height of the potential barriers between the wells, the rotation of the dipoles may be free or hindered. With no barriers the APES has a two-dimensional polar trough. In this case the dipoles are freely rotating with some angular frequency.

For perovskite crystals $\text{ABO}_3$ with a PJTE-induced eight-minimum APES at the B centers, the eight tunneling states were used to numerically solve the eigenvalue problem for the full Hamiltonian, including the PJT coupling and the effect of the applied electric field. The temperature-averaged response to the external electric field revealed the field dependent orientation polarization, dielectric susceptibility, and permittivity. Coinciding with a previous estimate by an order of magnitude, the orientation contribution to permittivity (which should not be there in the absence of the PJTE) is very large and (what was not shown before) it has a significant anisotropy. The origin of these effects was illustrated by a qualitative picture of what can be expected from the PJTE induced dipolar eight-minimum APES.

Explored in this paper, the PJTE includes vibronic coupling of HOMO to just LUMO, the excited $d$ orbitals of the central ion B. As it follows from the equation (2), the more opposite-parity excited states are coupled to HOMO, the more polar-flexible the ground state becomes and, correspondingly the stronger is the polar instability of the ion B. Distinguished from the simplest model of this paper, including other excited states adds more parameters of vibronic coupling, other $F$s and $\Delta$s. Their complex interplay may result in a somewhat change of wrapping of the ground-state trough. For example, as a plausible effect, instead of the eight-minimum shape of the trough there can be a six-minimum APES. As the most stable low-temperature ferroelectric phase this would determine the
tetragonal crystal structure. However, discussed in this paper orientation contribution in electric susceptibility in the high-temperature phase is the same in the six-minimum case as well. Similar to eight-minimum case it would result in a considerable enhancement of permittivity due to orientation polarizability of local dipoles in the external electric field.

The results above are obtained as functions of $\Gamma$ or the ratio $\Gamma/d_0$, where $\Gamma$ is introduced as the tunneling splitting parameter, and $d_0$ is the dipole moment in the minimum of the APES. The main parameter is the dipole moment $d_0$ that stands for the polar distortion, and hence it characterizes the magnitude of the observable effects. As for $\Gamma$, its main function is to stand for the speed of transitions between the minima which may vary significantly depending on the height of the energy barrier between them. With low barriers these transitions become more of over-the-barrier nature, and at a zero barrier they are free rotations along the PJTE-induced two-dimensional trough. All the conclusions of this paper apply to the case when over-the-barrier mechanism dominates over tunneling. The only expected difference is the activation nature of the corresponding temperature dependence of the orientation part of susceptibility in this case. Qualitatively, the effects described above in this paper will be present in all such cases, subject to the polar instability $d_0 > 0$, but the quantitative description may be different. The “rotation frequency” of the dipoles influences mostly the magnitude of the field at which the orientation polarization is saturated.

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[12] The axes for the molecular orbitals in the paper of Gomez et al [9] do not coincide with the \(x, y, z\) ones for the vector of dielectric induction \(D\). Therefore their matrix (4) is somewhat different from ours. Beside this in their equation (3.1) the minus sign is omitted.

[13] Traditionally for the polar angle \(\theta\) the reading is from the “north pole” where \(\theta = 0\) to the “south pole” with \(\theta = \pi\). In this paper the read-off value \(\theta = 0\) corresponds to the equatorial direction whereas the direction to the north pole is at \(\theta = \pi/2\), and to the south pole at \(\theta = -\pi/2\).

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