Off-center displacements of Ti ions in oxide ferroelectrics and a gigantic photo-induced dielectric constant of quantum paraelectric perovskite oxides in the electron-lattice theory

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Abstract. In this work we investigate the coupling of the $F_{u}$ vibrations with the actual electronic states of $BO_{6}^{n-}$ cluster in ABO ferroelectric-oxides. This coupling leads to the dynamical covalency hybridization of B(Ti,Ta,Nb) and oxygen electronic states. It is shown that at fulfillment of definite criteria the free energy at $T=0$, the adiabatic potential of $BO_{6}^{n-}$ cluster have the following configurations: 1) one maximum at $x_0 = y_0 = z_0 = 0$ (ferroelectric instability); 2) eight minima in the points $|x_0| = |y_0| = |z_0| = y_0$; 3) twelve saddle points at $|p| = |q| = 0$, $r = 0$ with a maximum in the $r$ cross-section and minima along $p$ and $q$. We show that the photo-induced changes of local ferroelectric distortions can take place. A gigantic enhancement of the dielectric constant by UV-light illumination is calculated in the electron-lattice theory in quantum paraelectrics of perovskite oxides, such as SrTiO$_3$ and KTaO$_3$, under a weak DC electric field. The temperature dependence of the gigantic real part of the dielectric constant $\varepsilon_{UVD}$ of SrTi$_3$O$_9$ under both UV-light and DC electric fields is calculated in satisfactory agreement with the experiment.

1. Introduction
In the electron-lattice (vibronic) theory (see for example [1-5]), the detailed structure of the electronic bands determines which kind of the ferroelectric transition occurs. The highest ground state and the lowest excited state play the leading role, as usually recognized for interband electron-lattice interactions. The ground state electronic band e.g. in BaTiO$_3$ is constructed with 2p(O)-type atomic wave functions, and the lowest excited state is due to 3d(Ti)-type atomic wave functions [6,7]. Thus, from the viewpoint of the electron-phonon interaction model, the origin of the ferroelectric structural phase transitions in BaTiO$_3$ is due to the dynamical electron-lattice p-d interaction (in PbTiO$_3$, the interband electron-phonon interaction with Pb 6s-state has also to be included) [2]. At zero temperature the valence band contains electrons and the conduction band is empty. These bands are mixed by lattice vibrations. In the case of ferroelectric oxides the active vibrations are $\Gamma_{15}(F_{u})$ TO-optical modes.

In [6,7] the calculations are carried out in local-density approximation (LDA) using the linearized augmented plane-wave (LAPW) for perovskite oxides. It was shown that the hybridization of oxygen 2p states and Ti 3d states leads to the ferroelectricity in BaTiO$_3$. However, in the LDA calculations this...
p-d hybridization is static. In the electron-lattice theory [1-4] 2p-3d hybridization (covalency) is dynamic. As we stated above reported first-principles band-structure calculations of perovskite oxides [6,7] has demonstrated that the p-d interaction is essential for the phase transitions in perovskites.

2. Adiabatic potential of TiO₆ cluster

Now we calculate the electronic states, which are renormalized by the electron-lattice interaction in perovskite oxides. In the next step we calculate off-center displacement of Ti ion in BaTiO₃, PbTiO₃ (in KNbO₃, e.g. the Ti ion is replaced by Nb ion, etc.). In this case the titanium ion is considered as a single impurity in the lattice. Following to the papers [5,8] we use cluster model molecular orbital (MO) description of the electronic structure of the TiO₆ cluster and the Madelung potential of the remaining crystal lattice (enlarging the cluster size does not change the qualitative results). It is obtained [5] the qualitative MO energy level scheme in figure 1. It is a typical MO LCAO scheme for octahedral transition metal d⁰ systems [8]. The ground state of the system A₁g [8] is formed by the occupied 12 oxygen 2pπ orbitals of F₁u, F₂g, F₁g and F₂u symmetry (F₁g and F₂u are not shown in figure 2 as unessential), while the lowest unoccupied MO consists of the three dπ(F₁g) orbitals (dₓz, dₓy, dᵧz) of Ti⁴⁺. The F₁g orbitals of Ti and O form π bonds which are weak as compared with the main σ bonds.

The off-center displacement of titanium with respect to the oxygen octahedron and the remaining crystal are of the three-fold degenerate F₁u(x,y,z) type. Under these displacements, only F₁g and F₂g states interact (become mixed). The secular equation for the electronic energies as a function of these ionic displacements ε(x,y,z), considering the linear terms of the electron-phonon interaction as a perturbation, is the 9th order (six 2pπ states of the oxygen forming F₁u and F₂g combinations and the three F₂g states of Ti). The secular equation is the following:

\[
\begin{vmatrix}
ε + δ & 0 & aᵧ & aₓ & 0 & 0 & 0 \\
0 & ε + δ & 0 & aₓ & 0 & 0 & 0 \\
aᵧ & aₓ & 0 & ε + δ₁ & 0 & V_{pₓ,y} & V_{pₓ,z} \\
aₓ & 0 & aₓ & 0 & ε + δ₁ & V_{pᵧ,y} & V_{pᵧ,z} \\
0 & aᵧ & 0 & 0 & ε + δ₁ & V_{pᵧ,x} & V_{pᵧ,z} \\
0 & aᵧ & 0 & 0 & ε + δ₁ & 0 & V_{pᵧ,x} \\
0 & 0 & V_{pₓ,y} & V_{pₓ,x} & 0 & ε - δ₂ & 0 \\
0 & 0 & V_{pᵧ,z} & V_{pᵧ,x} & 0 & ε - δ₂ & 0 \\
0 & 0 & 0 & V_{pᵧ,z} & V_{pᵧ,x} & 0 & ε - δ₂ \\
\end{vmatrix} = 0 \tag{1}
\]

where

\[
a = \langle p_x^+(O) \frac{\partial H}{\partial x} \rangle \bigg|_{\tilde{x}} \langle d_{xz}(O) \rangle, \tag{2}
\]

\[
V_{pₓ} = \langle p_x^+(O) \frac{\partial H}{\partial x} \rangle \bigg|_{\tilde{x}} \langle d_{xz}(Ti) \rangle \tag{3}
\]

In [5] it was supposed \(V_{pₓ} = a\) and roots of secular equation (1) \(ε_{±}^{pₓ} = ±\sqrt{δ^2 + a^2(x^2 + y^2)}\), \(ε_{±}^{pᵧ} = ±\sqrt{δ^2 + a^2(z^2 + a^2)}\), \(ε_{±}^{d_{x}} = ±\sqrt{δ^2 + a^2(ε_x^2 + ε_y^2)}\), \(ε_{4,5,6} = δ\), where 2δ is the average energy gap between 2pₓ(O) and 3d(Ti) states. In our opinion, these solutions are incorrect. These solutions are not satisfactory also from the general point of view because the symmetry of the free energy (adiabatic potential) in a cubic phase depends on the filling of electronic states and may be not cubic (the analogy with the Peierls transition is absent). The actual case \(V_{pₓ} >> a\) leads also to the another analytical solutions of secular equation (1) [2,4].
The secular equation (1) was solved numerically. In the ground state the lowest six of these nine one-electron states are populated by 12 electrons (figure 1), and together with the harmonic phonon part of the Hamiltonian \( H \) they form the adiabatic potential at \( T=0 \). It can be shown that from nine solutions of secular equation (1) three are positive ones, which are not populated and can be omitted. Then the adiabatic potential can be written as

\[
F(T = 0) = 2 \sum_{\sigma = 1}^{6} \varepsilon_\sigma(x, y, z) + \frac{1}{2} M \omega_0^2 (x^2 + y^2 + z^2),
\]

where \( \varepsilon_\sigma(x, y, z) \) are the negative solutions of equation (1), obtained numerically. The quantities \( M \) and \( \omega_0 \) are correspondingly the mass factor and bare frequency of the active vibrations.

Under certain conditions the surface (4) has the following extremum points (cf. [8]): 1) one maximum at \( x_0 = y_0 = z_0 = 0 \) (ferroelectric instability); 2) eight minima in the points \( |x| = |y| = |z| = y_0 \). Notice in the minimum points the Ti ion is displaced along the trigonal axes toward three oxygen atoms and away from the other three; 3) twelve saddle points at \( |p| = |q| = 0 \), \( r = 0 \) \( (p, q, r = x, y, z) \) with a maximum in the \( r \) cross-section and minima along \( p \) and \( q \). At these points the Ti ion is displaced toward two oxygen ions on the \( p \) and \( q \) axes; 4) six saddle points at \( p = q = 0 \), \( r \neq 0 \). From these calculations it follows that in perovskites only the rhombohedral configurations is expected to be stable and well ordered, as seen by experiment in [9]. However, another interpretation of the experiment in [9] is possible. We must take into account that only tetragonal ferroelectric phase in PbTiO\(_3\) is observed. The calculated energy \( F(T=0) \) as a function of Ti displacement (soft-mode distortion) in BaTiO\(_3\) for rhombohedral phase is given in figure 2. We use the parameters \( a=0.35 \text{ eV/Å}, V_{pd}=1.0 \text{ eV/Å}, M \omega_0^2=10.0 \text{ eV/Å}^2, \delta_1 = 1.43 \text{ eV}, \delta_2 = 1.51 \text{ eV} \) and \( \delta_3 = 1.43 \text{ eV} \) and obtain the free energy \( F(T=0) \) as a function of Ti displacement close to the calculated \( F(T=0) \) in BaTiO\(_3\) by a first principles calculations by Cohen [7]. In [7] the static hybridization of 2p O electronic states with 3d Ti states is responsible for ferroelectric distortion. In our calculations the dynamic hybridization of 2p O states with 3d Ti electronic states leads basically by 2p-3d electron-lattice coupling (\( V_{pd} \)) to the ferroelectric distortion.

\[\text{Figure 1. The MO energy level scheme for the TiO}_6^- \text{ cluster.}\]
Figure 2. The energy dependence of the Ti rhombohedral displacement relative to Ba in BaTiO$_3$. The solid curve is calculation by our theory, the dashed line is a first principles calculation by Cohen [7].

The TiO$_6^+$ cluster with off-center displacement of Ti and other ions also is important element of relaxor ferroelectricity.

Under light illumination according to the Eq. (4) with changing the electronic population of levels [10,11] the ferroelectric distortion diminishes up to 10%. In the strong laser field $V_{pd}$ increases and the ferroelectric distortions increases up to 10% and local photo-included ferroelectricity may occur.

3. Photoinduced effects on quantum paraelectrics

For a quantum paraelectric the dielectric constant equals [4]

$$\varepsilon = \frac{C_0}{T^2 + |T_c|^2},$$

where (supposing $a=0$)

$$T_c = \left[(AT_c^* - \lambda(0))r^{-1}\right]^{1/2},$$

$$T_c^* = A^{-1}\left(\frac{8V_{pd}^2}{\Delta} - M\omega_0^2 - \frac{B_0 - B_0'}{\sqrt{M}}\right).$$

Here $A$, $\lambda(0)$ and $r$ are the quantities which characterize the phonon-phonon interactions [4] including zero-point motion of atoms; $B_0$ and $B_0'$ are determined by the vertex corrections of the electron-lattice coupling to the soft mode, $\Delta$ is the average electronic gap [2]. The quantity $C_0 = \frac{4\pi\bar{e}^2}{v_f}$ in Eq. (5), where $v$ is the unit cell volume. The effective charge $\bar{e}$ contains contributions from the dynamical hybridization with the electronic order parameter

$$\langle a_{\sigma\delta}^T a_{\sigma\delta} \rangle_{\sigma=\sigma'} = \frac{1}{N_0} \sum_\delta \frac{V_{pd}(\bar{q})\langle y_\delta y_\delta \rangle + \langle y_\delta y_{\bar{q}} \rangle^{1/2}}{E_\sigma(k + \bar{q}) - E_\sigma(k)} \left[f_\sigma(k) - f_\sigma(k + \bar{q})\right],$$
where $N_0$ is the number of unit cells and $f_\sigma$ are the occupation numbers of electronic bands.

In both, UV light and DC electric fields, band-gap photoexcitations lead to the enhancement of the dielectric constant in SrTi$_{16}$O$_3$ and KTa$_{16}$O$_3$ according to our electron-lattice (vibronic) theory. The DC electric field causes a local breaking of inversion symmetry [12] and as a result it leads to the increase of the contribution from the intraband electron-phonon couplings ($V_{dd}(\tilde{q})$ and $V_{pq}(\tilde{q})$) into the dielectric constant (through $E_\sigma(\tilde{k} + \tilde{q})$ and $E_\sigma(\tilde{k})$ in Eq. (8)). If DC field is absent $V_{pp}(\tilde{q} \rightarrow 0) = 0$ $V_{dd}(\tilde{q} \rightarrow 0) = 0$ because of the symmetry rules (in the cubic phase the soft mode has the $F_{1u}$ symmetry).

Expanding $E_{\sigma,\sigma'}$ in power series relative to constants $V_{\sigma,\sigma'}$ in (8) we obtained for the dielectric constant the expression

$$\varepsilon_{\text{UVDC}} = \frac{4\pi}{\sqrt{\rho^2 + \rho^2}} \left( \tilde{\varepsilon}_0 + \left[ A + B J E_D^2 - C J^2 E_D^4 \right] \right)^2,$$

where the intensity of light field $J \sim E_r^2$; $E_r$ is the amplitude of laser field, $\tilde{\varepsilon}_0$ is the effective charge in the absence of the light irradiation and DC electric field $E_D$. For all the coefficients $A$, $B$ and $C$ entering Eq. (9) lengthy expressions have been obtained (with the use of papers [1-4]) containing the characteristics of bands, phonons and electron-lattice interactions.

The calculated dependence of the ratio $\varepsilon_{\text{UVDC}}/\varepsilon$ at 5 K on DC electric field $E_D$ at $J=8.2 \times 10^{13}$ photons/cm$^2$s is given in figure 3 in comparison with the experimental data [13-15]. The calculated dependence of the ratio $\varepsilon_{\text{UVDC}}/\varepsilon$ on the intensity under $E_D=40$ V/mm in comparison with the experimental data [13] is given in figure 4 (see also [16]).

![Figure 3](image-url). The dependence of $\varepsilon_{\text{UVDC}}/\varepsilon$ on the DC electric field under a constant UV irradiation of $1.6 \times 10^{15}$ photons/cm$^2$s, $\lambda=325$ nm. The solid curve is the theoretical one, solid circles are the experimental points [13].
Figure 4. The dependence of $\varepsilon_{UVDC}/\varepsilon$ on UV intensity under DC of 40 V/mm. The unit of intensity is $\times10^{16}$ photons/cm²s. The solid curve is the theoretical one, solid circles are the experimental data [13].

According to [14] the photo-induced enhancement of the dielectric constant can be observed only when the sample is illuminated, and it disappears promptly after stopping the illumination. Visible light below the band-gap energy (3.2 eV) does not induce such an enhancement. However, in defect subsystem the photo-induced dielectric enhancement in SrTiO₃ remains even after the photon is turned off, longly.

Acknowledgments
This work is supported by the Estonian Science Foundation grant No 6539.

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