Cluster *ab initio* modeling of local lattice instability in relaxor ferroelectrics

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The possibility of a zigzag type instability occurring for oxygen atoms in B–O–B, B–O–Nb, Nb–O–Nb linear chains is examined in disordered mixed perovskite compounds $\mathrm{Pb}(B_{1/3},\mathrm{Nb}_{2/3})\mathrm{O}_3$ (B = Mg, Zn, Cd). Local adiabatic potentials for oxygen atoms are studied using total energy calculations by *ab initio* Hartree–Fock + MP2 method for many-atomic clusters with different oxygen surroundings of lead atoms. The effect of lattice relaxation along the chain on a shape of the local potential in the transverse direction for the central oxygen atom is considered.

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1. Introduction

The disordered perovskite compounds of complex composition $\mathrm{Pb}(\mathrm{Mg}_{1/3},\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PMN), $\mathrm{Pb}(\mathrm{Zn}_{1/3},\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PZN), $\mathrm{Pb}(\mathrm{Cd}_{1/3},\mathrm{Nb}_{2/3})\mathrm{O}_3$ (PCN) belong to the class of the relaxor ferroelectrics. They have a broad, strongly frequency-dependent maximum in the temperature dependence of the dielectric permittivity and retain the average cubic symmetry down to 5 K [1–5]. To explain the unusual properties of relaxor ferroelectrics, a number of models have been proposed. For instance, the diffuse ferroelectric phase transition model by Smolenskii and Isupov [1,2,6], a dipolar glass model by Cross [7], random field induced domain state model by Westphal, Kleemann and Glinchuk [8] can be mentioned.

One of the main structural features of the mixed perovskites is the random occupation of the positions B in ideal perovskite lattice by the chemically different ions. This disorder gives rise to local distortions of cubic perovskite structure, that is, to random displacements of ions from the pseudocubic sites. Two types of such displacements are possible. First type displacements are determined simply by difference in ionic radii and valences and are frozen when random distribution of the ions is quenched. Such displacements of ions produce a set of random local dipoles, which are, in turn, the source of the random local electric field. In addition to this type of local distortions one can infer also the possibility of atomic displacements concerned with local lattice instabilities produced by peculiarities of chemical bonding in mixed perovskites [9,10]. These local polar distortions would be reversible and could play an important role in the formation of the ferroelectric micro regions in PMN, PZN and PCN along with the correlated displacements of polar optical type [11,12] frozen in the random local electric field.

One can expect that in the mixed perovskites oxygen ions could be unstable relative to off-center shifts in the plane parallel to pseudocubic face (the local zigzag instability in B–O–B' linear chain) [9,10]. The standard crystallographic analysis based on X-ray or neutron diffraction data [13,14] and pair-density function (PDF) analysis of pulsed neutron and synchrotron X-ray powder diffraction data [15] show that in PMN, oxygen off-center shifts in the planes parallel to the cube faces are equal to $\approx 0.17{-}0.19$ Å by [13,14] and to ≈ 0.4 Å by [15]. However, these methods cannot identify the origin of the observed oxygen shifts. Thus in [9,10] the cluster *ab initio* calculations of potential well for oxygen atom and of the equilibrium oxygen position in the B–O–Nb, B–O–B (B = Mg, Zn, Cd) and Nb–O–Nb chains in PMN, PZN, and PCN were performed. It was found that in B–O–Nb chains in PMN, PZN, PCN and in B–O–B chains in PZN, PCN oxygen atoms move in multi-well potentials with four minima shifted transversely to fourfold [001] axis. Whereas the oxygen atom in Nb–O–Nb chain in PMN, PZN, PCN and all oxygen atoms in BCN move in single-well potentials. This raises the question as to whether the solutions found in [9,10] are stable relative to the cluster size, atomic basis sets extensions, or a structural relaxation of the oxygen surroundings. These problems are studied in the present paper.

2. Method of calculations

Taking into account aperiodic structure of disordered relaxor ferroelectrics we used for the local potential wells calculations the quasi-molecular cluster *ab initio* method described in [16–18]. In cubic perovskite structure oxygen atoms are situated in centers of cubic faces, in the middle point between neighboring B cations forming in PMN, PZN and PCN Nb–O–Nb, B–Nb–B and B–O–Nb chains with B–O and Nb–O bonds of equal length. Therefore the crystalline surroundings of the oxygen atoms is modelled by one of the extended two-octahedron clusters $[\mathrm{O}B\mathrm{NbPb_4(OH)_{10}(OH_2)_8}]^{3+}$, $\mathrm{O}B_2\mathrm{Pb_4(OH)_{10}(OH_2)_8}$ or $[\mathrm{ONb_2Pb_4(OH)_{10}(OH_2)_8}]^{6+}$ instead of simple two-octahedron clusters $[\mathrm{O}B\mathrm{NbPb_4(OH)_{10}}]^{3+}$, $\mathrm{O}B_2\mathrm{Pb_4(OH)_{10}(OH_2)_8}$ or $[\mathrm{ONb_2Pb_4(OH)_{10}}]^{6+}$ used in [9,10]. The clusters consist of corner-shared octahedrons ($\mathrm{NbO_6}$ and $B\mathrm{O_6}$) and involve four Pb atoms (around the central oxygen) and eight additional oxygen atoms (around the lead atoms) arranged in the „mirror“ plane. In addition, hydrogen atoms are placed on broken bonds of surface oxygen atoms at the distance of 1 Å to reduce a net charge of the cluster. All interatomic distances are equal to corresponding values in ideal perovskite structure PMN with lattice constants $a_0 = 4.0278$ Å (PMN) [10], $a_0 = 4.04$ Å (PZN) [19], and $a_0 = 4.135$ Å (PCN) [20].

To find the local adiabatic potential for an atom in a crystal, one has to calculate the total energy of the crystal as a function of atomic displacement from the cubic perovskite lattice site position, assuming that the remaining atoms occupy their equilibrium positions in the crystal. A local adiabatic potential is defined as $\Delta E(\boldsymbol{\eta}) = E(\boldsymbol{\eta}) - E_0$, where E is a total crystal energy and $\boldsymbol{\eta}$ is a shift of the oxygen atom. A cluster approximation is used for the total energy: $\Delta E(\boldsymbol{\eta}) \cong \Delta E^{\mathrm{cl}}(\boldsymbol{\eta})$, where $E^{\mathrm{cl}}(\boldsymbol{\eta})$ is a total energy of a corresponding cluster.

Calculations of the electronic structure and total energy of the cluster are performed in the framework of *ab initio* restricted Hartree–Fock (RHF) MO LCAO method with 2nd order Møller–Plesset perturbation theory electron correlation corrections (MP2) to total energy, using the PC GAMESS version [21] of the GAMESS (US) QC package [22]. The following atomic gaussian basis sets have been used: WTBS basis sets $(27s, 20p, 17d)/[5s, 3p, 2d]$ for Nb, $(23s, 13p)/[3s, 1p]$ for Mg, $(27s, 20p, 17d)/[5s, 3p, 2d]$ for Zn and $(28s, 20p, 17d)/[5s, 3p, 2d]$ for Cd [23], TZV basis set $(10s, 6p)/[5s, 3p]$ for oxygen atom [24] with Pople $(2df, 2pd)$ polarization functions [25] for central oxygen atom and with DHMS polarization function [26] for other oxygen atoms, basis set $(4s)/[2s]$ for H [20] and basis set SBKJC ECP for Pb (Ba) [27].

3. Results and discussion

The results of cluster *ab initio* calculations of local adiabatic potentials for oxygen atoms in disordered relaxor ferroelectrics are presented in Figs. 1–5.

In Fig. 1 local potentials for the oxygen atoms along B–O–Nb (B = Mg, Zn, Cd) chains in PMN, PZN and PCN are presented. The equilibrium oxygen positions $z_{\min}$ are shifted from the middle point by 0.11 Å for PMN, by 0.12 Å for PZN and by 0.2 Å for PCN towards Nb atom. The shape of potential well along the chain is strongly influenced by electron correlation as in [9,10].

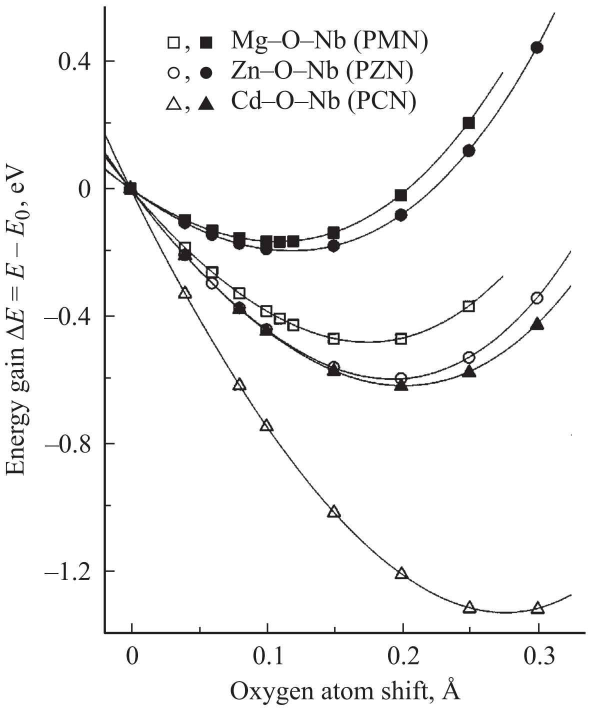

Figure 1. Local adiabatic potentials $\Delta E(0, 0, z)$ for oxygen atom in B–O–Nb chain along the chain in PMN, PZN and PCN, calculated by RHF method (open symbols) and by RHF + MP2 method (solid symbols). The oxygen shift from the middle point is positive in the direction of Nb atom.

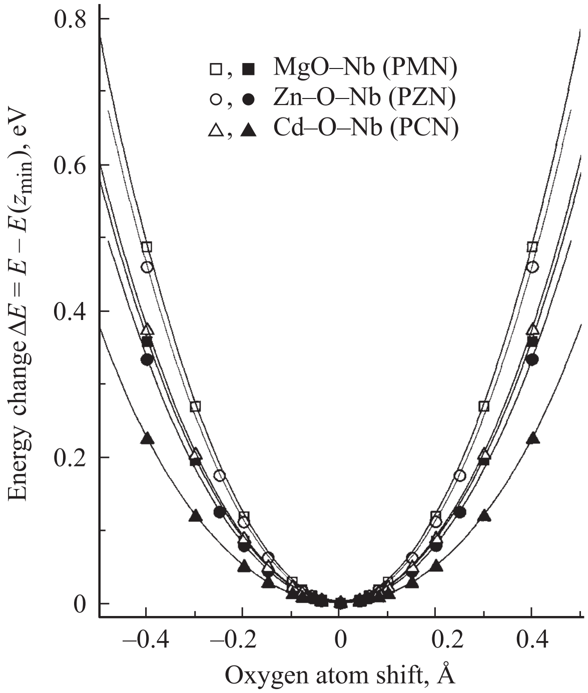

Figure 2. Local adiabatic potentials $\Delta E(x, 0, z_{\min})$ for oxygen atom in B–O–Nb chains in the transverse [100] and [010] directions in PMN, PZN and PCN, calculated by RHF method (open symbols) and by RHF + MP2 method (solid symbols).

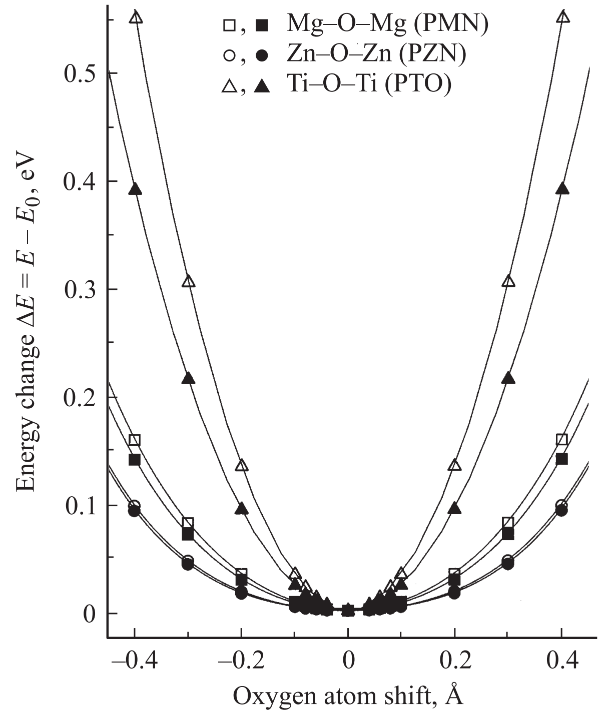

Figure 3. Local adiabatic potentials $\Delta E(x, 0, 0)$ for oxygen atoms in Mg–O–Mg and Zn–O–Zn chains in PMN and PZN and in Ti–O–Ti chain in PTO in the transverse [100] and [010] directions, calculated by RHF method (open symbols) and by RHF + MP2 method (solid symbols).

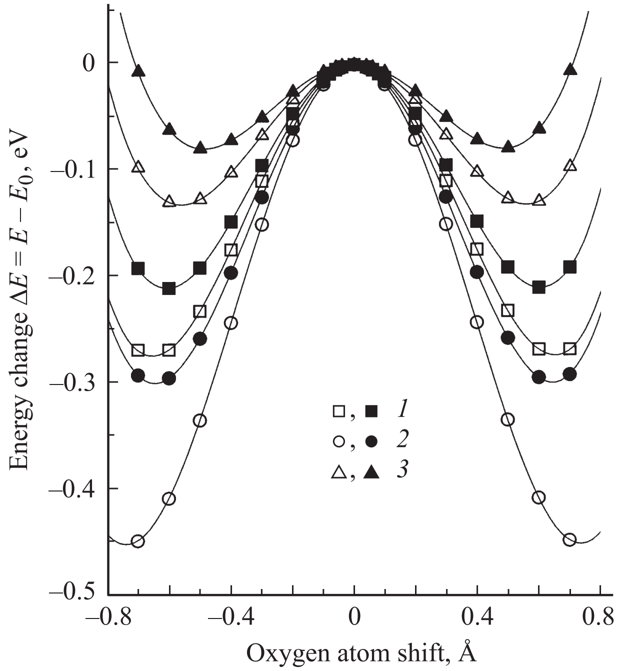

Figure 4. Local adiabatic potential $\Delta E(x, 0, 0)$ for oxygen atoms in Cd–O–Cd chain in PCN in the transverse [100] and [010] directions, calculated by RHF method (open symbols) and by RHF + MP2 method (solid symbols), for the cases *1–3*, described in the text.

In Fig. 2 local potentials for oxygen atoms in B–O–Nb (B = Mg, Zn, Cd) chains in the directions [100] and [010] transversal to the chain are presented for both PMN, PZN and PCN. As indicated in Fig. 2, the local potentials wells for oxygen in PMN, PZN and PCN are single-well, so that the central position of the oxygen in Mg–O–Nb chain in PMN and in Cd–O–Nb chain in PCN is stable in transverse direction.

In Fig. 3 local potential wells for the oxygen atoms in B–O–B (B = Mg, Zn) chains in the directions [100] and [010] transversal to the chains are presented for both PMN and PZN and similar local potential for oxygen in Ti–O–Ti chain for PTO. In the both cases oxygen atom moves in mirror plane in a soft single-well local potential with small transverse stiffness $\kappa_\perp$ (defined as $\kappa_\perp = 2\Delta E(\boldsymbol{\eta})/\eta^2$ at $\eta \to 0$) equal to 1.3 eV/Å^2 for PMN and to 0.65 eV/Å^2 for PZN within RHF + MP2. For comparison, the similar stiffness for oxygen in PTO is equal to 4.7 eV/Å^2. The anharmonic constants of the forth order are nearly the same for all three compounds.

In Fig. 4 local potentials for oxygen atoms in Cd–O–Cd chain in PCN in the directions [100] and [010] transversal to the chain are presented for three different cases: (*1*) for $\mathrm{OCd_2Pb_4(OH)_{10}}$; (*2*) for cluster $\mathrm{OCd_2Pb_4(OH)_{10}(OH_2)_8}$; (*3*) for cluster $\mathrm{OCd_2Pb_4(OH)_{10}(OH_2)_8}$ taking into account a lattice relaxation for Cd–O distances along the chain. In the first two cases all interatomic distances are equal to that for average cubic structure. In the third case all distances are kept equal to their average values with the exception of Cd–O distances along the chain which are picked equal to $(a_0 + z_{\min})/2 = 2.1675$ Å where $a_0 = 4.135$ Å is the average lattice constant and $z_{\min} = 0.2$ Å is the shift of the oxygen atom in Cd–O–Nb chain from the mirror plane towards Nb atom. It is obvious from the curves that in all cases the oxygen atom in the Cd–O–Cd chain moves in the multi-well local potential with four minima shifted in transverse directions.

In Fig. 5 the local potentials in the mirror plane for oxygen atom in Nb–O–Nb chains in PCN and for Ti–O–Ti chain in PTO are presented.

Let us discuss the results. From comparison of the results presented in Fig. 2 with those found in [10] one can see that the inclusion of the additional eight oxygen atoms around lead atoms dramatically change the shape of the local potentials for oxygen atoms in the Mg–O–Nb, Zn–O–Nb and Cd–O–Nb chains in the directions transverse to the chains. We have obtained the single-well hard local potentials instead of multi-well potentials found in [10]. On the other hand, when the results presented in Figs. 3, 4 are compared with those found in [9,10], it is apparent that the shapes of the local potentials for oxygen atoms in Mg–O–Mg, Zn–O–Zn and Cd–O–Cd chains retain their qualitative features (the softness in the cases of Mg–O–Mg, Zn–O–Zn and the multi-well character in the case of Cd–O–Cd) being altered only quantitatively. We see also that the extension of the cluster increases the transverse harmonic stiffness for oxygen atoms as well as

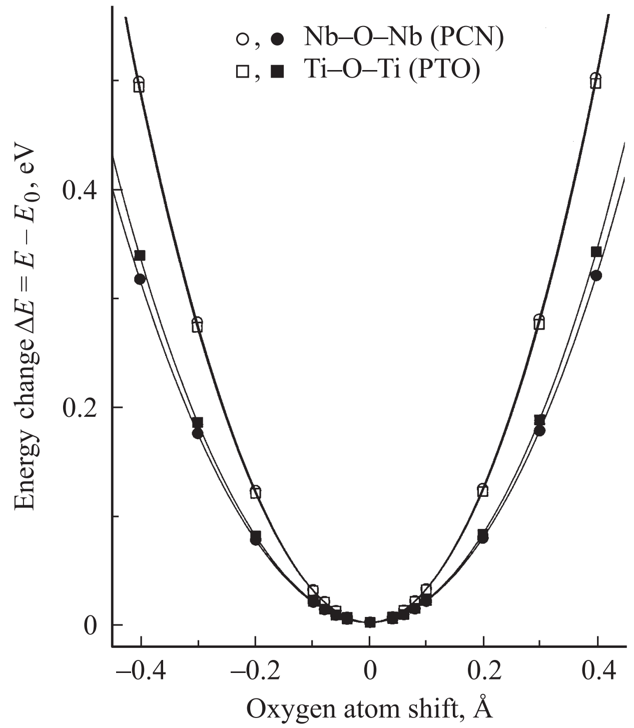

Figure 5. Local adiabatic potential $\Delta E(x, 0, 0)$ for oxygen atoms in Nb–O–Nb chains in PCN and in Ti–O–Ti chain in PTO in the transverse [100] and [010] directions, calculated by RHF method (open symbols) and by RHF + MP2 method (solid symbols).

taking into account the increase in Cd–O distance relative to average bond length.

It should be stressed that the availability of multi-well potentials for oxygen atoms in Cd–O–Cd chain gives a new mechanism of dipole ordering and of dielectric relaxation of order–disorder type in PCN. The softness of the transverse local potentials for oxygen atoms in Mg–O–Mg chain in PMN and in Zn–O–Zn chain in PZN (Fig. 3) may strongly influence on the ferroelectric state observed in these compounds after cooling in electric field [28,29]. Besides, the small transverse local stiffness for oxygen atoms in these chains may be responsible for large off-center shifts of the oxygen atoms in the planes parallel to cubic faces observed in [13–15]. Within classical statistics one can write a displacement of oxygen atom in the mirror plane due to thermal motion as $r_\perp = (\langle \mathbf{r}_\perp^2 \rangle)^{1/2} = (2T/\kappa_\perp)^{1/2}$. Taking into account the values of $\kappa_\perp$ calculated for PMN (1.3 ev/Å^2), PZN (0.65 eV/Å^2) and PTO (4.7 eV/Å^2) we find at $T = 300$ K that $r_\perp \approx 0.2$ Å in PMN (comparable with the observed values [13,14]), $r_\perp \approx 0.3$ Å in PZN and $r_\perp \approx 0.1$ Å in PTO. One should also take into account that displacement $r_\perp$ induced by an electric field $E_\perp$ is proportional to $E_\perp/\kappa_\perp$. This gives rise to larger difference in $r_\perp$ than in the case of thermal motion and results ultimately in much larger contribution into the induced polarization in PZN than in PMN.

4. Conclusion

We have studied local lattice instabilities for oxygen atoms in PMN, PZN and PCN employing cluster ab initio total energy calculation within restricted Hartree–Fock MO LCAO method with 2nd order Møller–Plesset perturbation theory electron correlation corrections. The influence of the oxygen surroundings of the lead atoms in the many-atomic clusters used for the *ab initio* simulation on the shape of local adiabatic potentials is considered. It is found that for oxygen atoms in the B–O–Nb chains (B = Mg, Zn, Cd) the use of extended cluster with eight additional oxygen atoms around lead atoms instead of simple two-octahedron cluster dramatically change the shape of potential curves in the planes parallel to cubic faces from multi-well to single-well type. At the same time, it is found that the shape of the local potentials for oxygen atoms in Mg–O–Mg, Zn–O–Zn and Cd–O–Cd chains is altered only quantitatively. The local potentials in directions transverse to the chain retain the softness in the cases of Mg–O–Mg, Zn–O–Zn and the multi-well character in the case of Cd–O–Cd.

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