Computer modelling of point defects in ABO_3 perovskites and MgO

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Abstract

We present results for basic intrinsic defects: F-type electron centers (O vacancy which trapped one or two electrons) and hole polarons bound to Mg or K vacancy in ionic MgO and partly covalent $KNbO_3$ perovskite, respectively. We demonstrate that a considerable covalency of the perovskite chemical bonding makes the F-type centers therein much more similar to defects in partly-covalent quartz-type oxides rather than the conventional F centers in alkali halides and ionic MgO. Both one-site (atomic) and two-site (molecular) polarons are expected to coexist in $KNbO_3$ characterized by close absorption energies. Our calculations confirm existence of the self-trapped electron polarons in $KNbO_3$, $KTaO_3$, $BaTiO_3$, and $PbTiO_3$ crystals. The self-trapped electron is mostly localized on B-type ion due to a combination of breathing and Jahn–Teller modes of nearest six oxygen ion displacements. The relevant lattice relaxation energies are typically 0.2–0.3 eV, whereas the optical absorption energies 0.7–0.8 eV, respectively. According to our calculations, the absorption energy of a bound electron polaron in $KNbO_3$ by 0.1 eV exceeds that for the self-trapped electron polaron and equals 0.88 eV.
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1. Introduction

Most of real crystals are non-stoichiometric and thus contain along with impurities large concentrations of intrinsic defects—vacancies. Oxygen vacancies are known to give rise to F^+ and F centers (vacancy which trapped one or two electrons, respectively) [1]. The properties of F-type centers in ionic oxides like MgO and α-Al_2O_3 are well studied, unlike $KNbO_3$ perovskite where up to now there exists only a tentative assignment of the electron-induced absorption band at 2.7 eV to the F-type centers [2]. In its turn, cation vacancies are able to trap radiation-induced holes. Thus, in irradiated MgO a cation vacancy is known to trap one or two holes giving rise to the V^- and V^0 centers [1,3] called bound hole polaron and

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bipolaron, respectively. In the V^- center a hole is trapped by one of the O^{2-} ions neighboring to the cation vacancy, thus creating an O^- paramagnetic ion, and a broad absorption band at 2.3 eV. The trapping of another hole on the opposite side of the vacancy results in a singlet spin state ($S = 0$) and a slightly perturbed V^- type absorption band.

Since the middle of seventies a number of theoretical studies were performed which aimed at understanding the properties of hole centers in oxides. It was shown that the mentioned absorption band at 2.3 eV in MgO corresponds to a small-polaron transition characterized by a hole transfer from a single O^- to the equatorial O^{2-} neighboring ions, at a frozen lattice configuration. The key factor in a hole localization on a single O^{2-} ion lies in the asymmetric displacement of one of six (otherwise equivalent) oxygens from a regular lattice site. This displacement was calculated later using the classical shell model (SM) as implemented into the HADES code. These calculations have, however, several limitations: (i) the assumption that a hole is entirely localized on a single oxygen ion; (ii) the short-range interaction between O^- and surrounding ions is assumed to be the same as for a regular O^{2-} ion. These limitations could be avoided by using larger quantum clusters with self-consistent treatment of the electronic/atomic structure and hole density distribution. For this purpose semiempirical quantum chemical methods are well suited.

2. INDO method

The updated intermediate neglect of the differential overlap (INDO) method [4–6] is a semiempirical version of the Hartree–Fock method. We recently applied this method to the study of phase transitions and frozen phonons in $KNbO_3$ [7], pure and Li-doped $KTaO_3$ [8], solid perovskite solutions $KNb_xTa_{1-x}O_3$ [9,10], as well as electron polarons in $BaTiO_3$ [11] and $PbTiO_3$ [12]. More details about the INDO method are given in Refs. [4–6]. In present calculations we use a periodic, the so-called large unit cell (LUC)

model. In this model the electronic structure calculations are performed for an extended unit cell at the wave vector $\mathbf{k} = 0$ in the narrowed Brillouin zone (BZ) which is equivalent to a band-structure calculation at several special points of the normal BZ, transforming to the narrow BZ center after the corresponding extension of the primitive unit cell.

The detailed analysis of the development of the INDO parameterization for pure $KNbO_3$ and $KTaO_3$ is given in Refs. [7,8]. The INDO method reproduced very well both available experimental data and results of ab initio LDA-type calculations. In particular, this method reproduces the effect of a ferroelectric instability of $KNbO_3$ due to off-center displacement of Nb atoms from the regular lattice sites, as well as the relative magnitudes of the relevant energy gains for the [1 0 0], [1 1 0] and [1 1 1] Nb displacements, which are consistent with the order of the stability of the tetragonal, orthorhombic and rhombohedral ferroelectric phases, respectively, as the crystal temperature decreases. This is a very non-trivial achievement since the typical energy gain due to the Nb off-center displacement is of the order of magnitude of several mRy per unit cell. The calculated frequencies of the transverse-optic (TO) phonons at the Γ point in the BZ of cubic and rhombohedral $KNbO_3$ and the atomic coordinates in the minimum energy configuration for the orthorhombic and rhombohedral phases of $KNbO_3$ are also in good agreement with experiment, thus indicating that a highly successful INDO parameterization has been achieved. The frozen-phonon calculations for T_{1u} and T_{2u} modes of cubic $KTaO_3$ are also in good agreement with experiment. The advantage of the INDO which is a semi-empirical version of the Hartree–Fock method, is that it allows to calculate the excited states of crystals and defects, and thus to obtain accurately the absorption and luminescence energies as the difference of the total energies for the ground and excited state (Δ SCF method). For example, the INDO calculated optical gap of $KNbO_3$ (which was not used in the INDO parameterization) is very close to the experimental (3.3 eV) in contrast to the DFT-calculated gap of 1.4 eV.

3. Quantum chemical modelling of F centers in KNbO₃ perovskite

In the KNbO$_3$ cubic phase all O atoms are equivalent and have the local symmetry C_{4v} (due to which the excited state of the F-type centers could be split into a non-degenerate and a doubly-degenerate level). The optimized atomic relaxation around the F center indicates an outward shift of the two Nb neighbors to the O vacancy by 3.9% which is associated with a lattice relaxation energy of 1.35 eV. This is quite close to the ab initio FP LMTO calculations (the Nb relaxation of 3.5% was accompanied by an energy gain of 0.5 eV, see Ref. [13]).

The outward relaxation of nearest K atoms and inward displacements of O atoms are much smaller. They give ≈20% of the net relaxation energy. The F center local energy level lies approximately 0.6 eV above the top of the valence band. Its molecular orbital contains primarily the contribution from the atomic orbitals of the two nearest Nb atoms. Only ≈0.6 e resides at the orbitals centered at the vacancy site, with the same amount of electron density localized at the two nearest Nb atoms. Hence the electron localization at the vacancy is much smaller than is known for F centers in ionic oxides. This difference could be due to the fact that the electrostatic (Madelung) field potential on a O site in KNbO$_3$ is much smaller than in ionic MgO (10.47 eV vs. 23 eV) and an electron is respectively less bound.

For the charged F$^+$ center the relaxation energy of 2.23 eV and the Nb displacements of 5.1% are larger than those for the F center due to a stronger Coulomb repulsion between unscreened O vacancy and Nb atoms: the share of the electron density inside the O vacancy decreases to 0.3 e. The calculated optical absorption energies for the F$^+$ and F centers are 2.30, 2.63 eV and 2.68, 2.93 eV, respectively. That is, both defects are predicted to have one of the bands around 2.6–2.7 eV in agreement with the experimental observation [2].

4. Modelling of hole polarons

4.1. KNbO₃

We found two energetically favourable atomic configurations in KNbO$_3$ in which a hole is well localized: one-site and two-site polarons (Fig. 1). In the former case the O$^-$ ion is displaced towards the K vacancy by 3% a_0. Simultaneously, 11 other oxygens surrounding the vacancy are slightly displaced outwards. The relevant lattice relaxation energy caused by atomic displacements is 0.4 eV (Table 1). In the one-site polaron the hole—like in MgO—is well localized by a single oxygen ion. The molecular orbital of the relevant local state contains a certain small contribution from atomic orbitals of other O ions, but not K or Nb ions, 80% of the spin density is localized on the displaced O$^-$ atom. In agreement with the generally
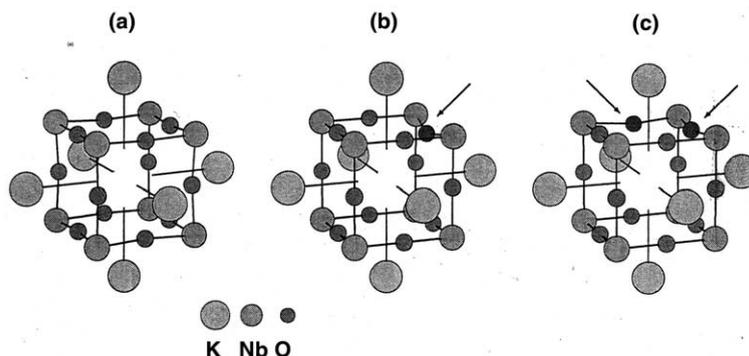

Fig. 1. Uniform relaxation of O atoms around the K vacancy in KNbO₃ (a) and the relaxation corresponding to the formation of one-site (b) and two-site (c) bound hole polarons. Arrows in (b) and (c) indicate the displaced O atoms.

Table 1
Optical absorption (E_{abs}) and lattice relaxation (E_{rel}) energies calculated for the hole centers in MgO and KNbO$_3$

Energy (eV) method	MgO INDO	KNbO$_3$ INDO	KNbO$_3$ FP LMTO [14]
E_{abs}	2.20 (2.30)[a]	0.95[a]	
	2.18 (2.30)[b]	0.98[c]	
E_{rel}	0.80[a]	0.40[a]	0.14[a]
	1.60[b]	0.53[c]	0.18[c]

FP LMTO is the ab initio method of full potential linearized Muffin Tin Orbitals. Experimental data for MgO [1,3] are given in brackets.

[a] Stands for one-site polaron.
[b] For bi-polaron.
[c] For two-site (molecular) polaron.

accepted polaronic model, the optical absorption energy of ≈ 1 eV corresponds to a hole transfer to the state delocalized over nearest oxygens.

In the two-site (molecular) polaron the two oxygens sharing a hole approach each other by 3.5% of the O–O distance (Fig. 1) in a perfect lattice, and its center of mass is displaced towards the K vacancy by 2.2%. Other 10 nearest O ions are displaced outwards the K vacancy, like the one-site hole case. The calculated absorption energy is quite close to that for the one-site polaron (Table 1). The two-site polaron in KNbO$_3$ is slightly lower in energy than the one-site polaron. This is in agreement with recent ab initio FP LMTO calculations [14].

4.2. MgO

The optimized geometry of the V$^-$ center (Fig 2a) shows that the O$^-$ ion, on which 80% of the hole density is localized, is displaced towards the cation vacancy by 3% of the interionic, Mg–O distance (2.1 Å). The displacements of other atoms are insignificant. The effective charges of the ions in a perfect crystal (± 1.85 e) confirm high ionicity of MgO. We found that the optical absorption of this defect is due to the charge transfer from the O$^-$ ion to equatorial O^{2-} ions, as it was described in a model [15,16]. The calculated optical absorption energy of 2.2 eV is close to the experimental value (Table 1). For the V^0 center shown in Fig. 2b, we have found that the minimum energy corresponds to the two holes sitting on the opposite sides of the Mg vacancy, in agreement with
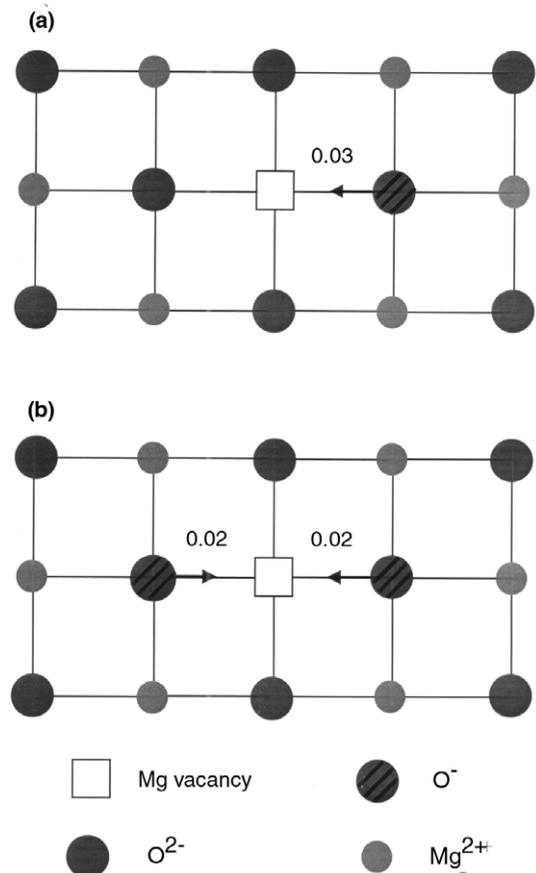

Fig. 2. A fragment of the MgO lattice around the (a) V$^-$ and (b) V^0 centers. The numbers show the calculated O$^-$ ion displacements (in units of the Mg–O distance).

experiment, which is accompanied by 2% displacement of the two relevant O$^-$ ions. The

calculated absorption energy is close to that for the V^- center and experiment (Table 1).

5. Self-trapped electron polaron

As an extension of the hole polaron study, we have modeled the *self-trapped electron* polaron in a cubic phase of $KNbO_3$. We used the $2 \times 2 \times 2$ extended cubic cell with the LUC containing 40 atoms. We allowed six nearest oxygen atoms in the octahedron around a central Nb atom in $KNbO_3$

to relax, in order to find the energy minimum of the system. All other Nb and K atoms, as well as the rest of O atoms in most cases were kept fixed at their perfect lattice sites (see below).

According to our INDO calculations, initially the polaron ground state is three-fold degenerate (t_{2g}). This degeneracy is lifted as a result of the combination of the breathing mode and the Jahn–Teller effect: 1.4% a_0 *outward* displacement of four nearest equatorial O atoms (with the energy gain of 0.12 eV) and *inwards* 1% a_0 relaxation of the two oxygens along the z direction (an additional

Table 2
Optical absorption and the relevant lattice relaxation energies (in eV) of electron polarons in ABO_3 perovskites as calculated by means of the INDO method

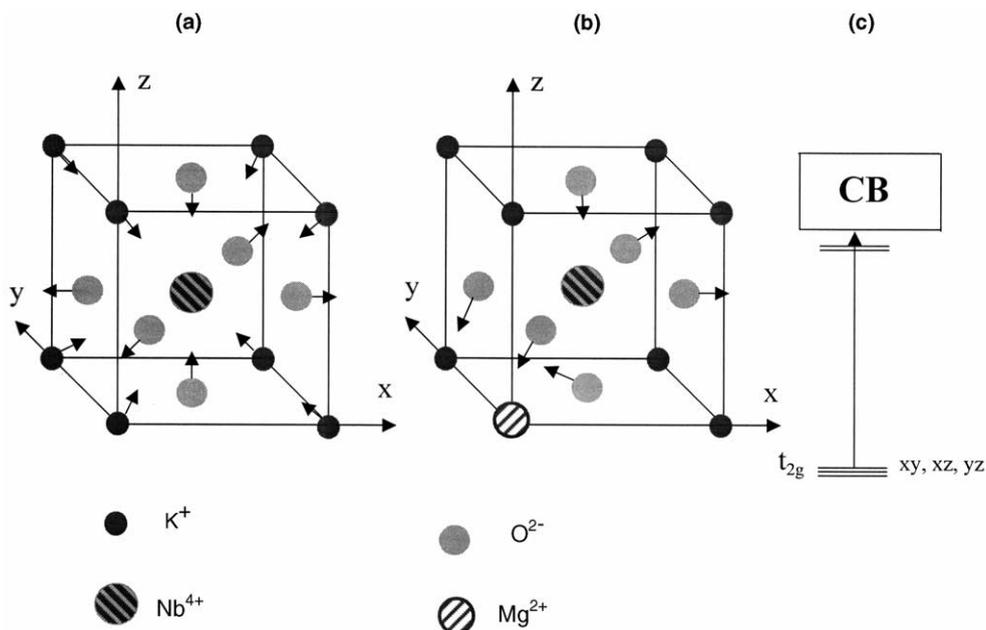| Electron polaron absorption and lattice relaxation energies in ABO_3 perovskites			
Crystal	Type of polaron	Absorption energy (eV)	Relaxation energy (eV)
$KNbO_3$	Electron polaron	0.78	0.21
	Bound electron polaron	0.88	0.36
$BaTiO_3$ [11]	Electron polaron	0.69	0.24
$KTaO_3$ [18]	Electron polaron	0.75	0.27
$PbTiO_3$ [12]	Electron polaron	0.73	0.22

Fig. 3. (a) Sketch of the asymmetric relaxation of 14 atoms around an electron localized on the central Nb atom in the self-trapped electron, (b) the same for bound electron polaron, (c) local energy levels within the gap.

gain of 0.09 eV). That is, the total lattice energy gain is 0.21 eV. A similar JT electron polaron was recently observed by means of ESR in $BaTiO_3$ [17].

Calculations show that a considerable (0.5 e) electron density is localized on the central Nb atom producing three closely spaced energy levels in the band gap. They consist mainly of the *xy*, *xz* and *yz* Nb 4d atomic orbitals (splitted t_{2g} energy level in an isolated ion) whereas two more empty levels are located close to the conduction band bottom. The electron polaron absorption energy was found to be 0.78 eV. We calculated this as the difference of the total, self-consistent energies for the ground and excited states (the Δ SCF method). The relevant absorption process corresponds to an electron transfer to the nearest Nb atom. This lies also in the same energy range as our previous electron polaron calculations in ABO_3, see Table 2. As to the energetics of the self-trapped electron formation process, previous ab initio LMTO calculations [7] have demonstrated that the bottom of $KNbO_3$ conduction band has a narrow subband which probably permits the electron localization energy to be small enough for a positive total self-trapping energy balance.

In this paper, we have studied additionally the effect of other atom relaxation, first of all, 8 K atoms which are NN for Nb. Results are shown qualitatively in Fig. 3a. Briefly, the additional lattice energy gain is only 0.02 eV, considerably smaller than the contribution from the asymmetrical relaxation of the 6 NN O atoms. Our experience with the F center comparative calculations for cubic and orthorhombic phases [13] clearly demonstrated that the optical absorption energies depend very weakly on the particular para/ferroelectric phase, because the lattice deformation energy around point defects is much larger than that for the tiny deformation due to the phase transition. We believe, this is also the case for the polarons under study.

6. Bound electron polaron

Along with the self-trapped (intrinsic) electron polaron discussed above, we have also modeled the electron polaron (Nb^{4+}) bound to the *nearest*

neighbor Mg^{2+} impurity (Fig. 3b). As initial guess, we used the atomic configuration for the self-trapped electron polaron described above. However, the Coulomb field of Mg impurity results in a considerable additional relaxation of three O atoms nearest to both Nb and Mg ions. The optimized displacements of these three O atoms directed towards the Mg atom along the relevant cubic faces are 1.84% a_0 and gives an additional 0.15 eV energy gain to already existing 0.21 eV relaxation energy. It means that a total relaxation energy turns out to be 0.36 eV, i.e., the bound electron polaron is more stable than the self-trapped electron polaron.

As a result of asymmetric O relaxation, similarly to a self-trapped electron polaron, around 0.5 e is localized on the central Nb atom. In the bound electron polaron the degeneracy of Nb 4d atomic orbitals, having t_{2g} symmetry and consisting mainly of Nb $4d_{xy}$, d_{xz} and d_{yz} atomic orbitals, where an electron polaron is localized, is lifted (Fig. 3c). According to our calculations, the absorption energy of a bound electron polaron by 0.1 eV exceeds that for the self-trapped electron polaron and equals 0.88 eV (Table 2).

7. Conclusions

We have demonstrated in this paper that modern large-scale computer modelling of complicated advanced materials is a very efficient tool for understanding their properties. Based on our quantum chemical INDO calculations of the optical properties of the F centers and hole polarons in $KNbO_3$, we confirm their tentative experimental assignments [2,19,20]. We demonstrate that a considerable covalency of the perovskite chemical bonding makes the F-type centers therein much more similar to defects in partly-covalent quartz-type oxides rather than the conventional F centers in ionic alkali halides and MgO. Our calculations confirm existence of the self-trapped electron polarons in $KNbO_3$, $KTaO_3$, $BaTiO_3$, and $PbTiO_3$ crystals. The self-trapped electron is mostly localized on B-type ion due to a combination of breathing and Jahn–Teller modes of nearest six oxygen ion displacements.

Despite the fact that the lattice relaxation gain in the INDO calculations is typically smaller than that ab initio calculated (see e.g., Table 1) the optical absorption energy for the hole polarons in MgO are close to the experimental data (Table 1) which allows to estimate the accuracy of the INDO calculations as 0.1–0.2 eV. This is more than enough for the qualitative conclusions made in our paper.

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