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### BRIEF REPORTS

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#### First-principles and semiempirical calculations for bound-hole polarons in KNbO<sub>3</sub>

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The *ab initio* linear muffin-tin-orbital formalism and the semiempirical method of the intermediate neglect of the differential overlap based on the Hartree-Fock formalism are combined for the study of the hole polarons (a hole trapped nearby the cation vacancy) in a cubic phase of KNbO<sub>3</sub> perovskite crystals. The 40-atom and 320-atom supercells were used, respectively. We predict the existence of both one-site and two-site (molecular) polarons with close optical absorption energies (0.9 eV and 0.95 eV). The relevant experimental data are discussed. [S0163-1829(99)12725-5]

#### I. INTRODUCTION

It is well understood now that *point defects* play an important role in the electro-optical and nonlinear optical applications of KNbO<sub>3</sub> and related ferroelectric materials.<sup>1</sup> In particular, reduced KNbO<sub>3</sub> crystals containing oxygen vacancies reveal fast photorefractive response to short-pulse excitations which could be used for developing fast optical correlators.<sup>2</sup> The prospects of the use of KNbO<sub>3</sub> for the light frequency doubling are seriously affected by the presence of unidentified defects responsible for induced infrared absorption.<sup>3</sup> The photorefractive effect, important in particular for holographic storage, is also well known to depend on the presence of impurities and defects. Most of the as-grown ABO<sub>3</sub> perovskite crystals are nonstoichiometric and thus contain a considerable amount of vacancies.

The so-called *F* and *F*<sup>+</sup> centers (an O vacancy, V<sub>O</sub>, which traps two or one electron, respectively),<sup>4-6</sup> belong to the most common defects in oxide crystals. In electron-irradiated KNbO<sub>3</sub>, a broad absorption band observed around 2.7 eV at room temperature has been tentatively ascribed to

the *F*-type centers.<sup>7</sup> These two defects were the subject of our recent *ab initio* and semiempirical calculations.<sup>8,9</sup> A transient optical absorption band at 1.2 eV has been associated recently,<sup>10</sup> in analogy with other perovskites, with a hole polaron (a hole bound, probably, to a K vacancy). The electron spin resonance study of KNbO<sub>3</sub> doped with Ti<sup>4+</sup> gives a proof that holes could be trapped by such negatively charged defects.<sup>11</sup> For example, in BaTiO<sub>3</sub>, the hole polarons bound to Na and K alkali ions replacing Ba, and thus forming a negatively charged site attracting a hole,<sup>12</sup> have also been found. Cation vacancies are the most likely candidates for pinning polarons. In irradiated MgO, they are known to trap one or two holes giving rise to the V<sup>-</sup> and V<sup>0</sup> centers<sup>4,5</sup> which are nothing but bound hole polarons and bipolarons, respectively. The results of the experimental studies of hole polarons in alkali halides and ferroelectric perovskites reveal two different forms of atomic structure of polarons: atomic one (one-site), when a hole is localized on a single atom, and molecular-type (two-site), when a hole is shared by two atoms forming a quasimolecule.<sup>11-13</sup> In the present study, we simulate hole polarons associated with a K vacancy in

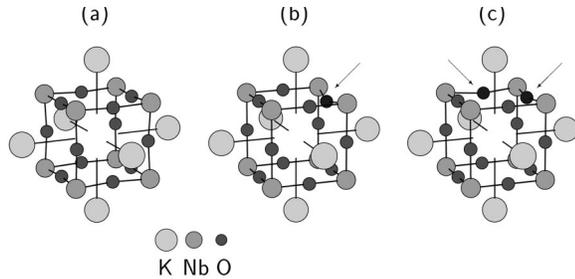


FIG. 1. Uniform relaxation of O atoms around the K vacancy in  $\text{KNbO}_3$  (a) and the relaxation corresponding to the formation of one-site (b) and two-site (c) polarons. Arrows in (b) and (c) indicate the displaced O atoms.

$\text{KNbO}_3$ , using an *ab initio* density functional theory (DFT)-based method in combination with a semiempirical treatment based on the Hartree-Fock (HF) formalism, employing the periodic boundary conditions and the supercell geometry in both cases.

## II. METHODS

The motivation for using the DFT-based and HF-based calculation methods in parallel is to combine strong sides of both in a single study. The DFT is expected to be able to provide a good description of the ground state, i.e., to deliver reasonable relaxation energies and ground-state geometry. In the HF approach, the relaxation energies are generally less accurate because of the neglect of correlation effects. On the other hand, the HF formalism is straightforwardly suited for the evaluation of excitation energies, because the total energies can be calculated for any (ground-state or excited) electronic configuration on equal footing, which is generally not the case in the DFT. Practical experience shows that HF and DFT results often exhibit similar qualitative trends in the description of dielectric properties but quantitatively lie on opposite sides of experimental data, thus effectively setting error bars for a theoretical prediction.<sup>14</sup>

Our *ab initio* DFT treatment is based on the full-potential linearized muffin-tin orbital (LMTO) formalism, previously applied with success to the study of structural instability and lattice dynamics in pure  $\text{KNbO}_3$ .<sup>15,16</sup> For the study of defects, we used the version of LMTO as implemented by van Schilfgaarde and Methfessel,<sup>17</sup> which was earlier used in our simulations for the *F* center in  $\text{KNbO}_3$  (Ref. 9; see also for more details of the calculation setup there). The exchange correlation has been treated in the local density approximation (LDA), as parametrized by Perdew and Zunger.<sup>18</sup> The supercell LMTO approach has been earlier successfully used for the simulation of defects in KCl (Ref. 19) and  $\text{MgO}$ .<sup>20</sup> In the present case we used the  $2 \times 2 \times 2$  supercells, i.e., the distance between repeated point defects was  $\approx 8 \text{ \AA}$ . As a consequence of the large number of eigenstates per  $\mathbf{k}$  point in a reduced Brillouin zone (BZ) of the supercell and of the metallicity of the doped system, it was essential to maintain a quite dense mesh for the  $\mathbf{k}$  integration by the tetrahedron method over the BZ. Specifically, clear trends in the total energy as a function of atomic displacements were only established at  $10 \times 10 \times 10$  divisions of the BZ (i.e., 186 irreducible  $\mathbf{k}$  points for a one-site polaron).

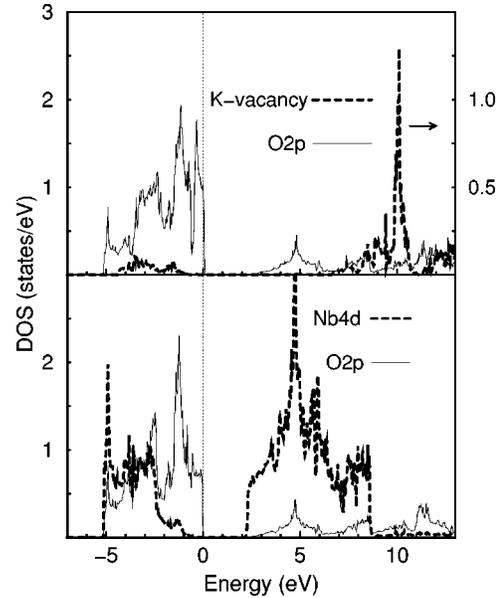


FIG. 2. Local DOS at the K vacancy site and at the adjacent oxygen atom (top panel) and at Nb and O sites in perfect  $\text{KNbO}_3$  (bottom panel), as calculated by LMTO.

In the HF formalism, a semiempirical intermediate neglect of the differential overlap (INDO) method,<sup>21</sup> modified for ionic and partly ionic solids,<sup>22,23</sup> has been used. The INDO method has been successfully applied for the simulation of defects in many oxides.<sup>8,9,24–27</sup> The calculations have been performed with periodic boundary conditions in the so-called large unit cell (LUC) model,<sup>28</sup> i.e., for  $\mathbf{k}=0$  in the appropriately reduced BZ. When mapped on the conventional BZ of the compound in question, this accounts for the band dispersion effects and allows to incorporate effectively the  $\mathbf{k}$  summation on a relatively fine mesh over the BZ. Due to the robustness of the summation procedure, the total energy dependence on the atomic displacements was found to be satisfactorily smooth for any supercell size (one should keep in mind, however, that the numerical results may remain somehow dependent on the LUC in question). In the present work,  $4 \times 4 \times 4$  supercells (320 atoms) were used, which is the extension of our preliminary INDO study<sup>29</sup> with the  $2 \times 2 \times 2$  supercells. The detailed analysis of the INDO parametrization for  $\text{KNbO}_3$  is presented in Ref. 30, and the application of the method to the *F*-center calculations is found in Refs. 8 and 9.

We restricted ourselves to a cubic phase of  $\text{KNbO}_3$ , with the lattice constant  $a_0 = 4.016 \text{ \AA}$ . In the vacancy-containing supercell, the relaxation of either one (for the one-site polaron) or two (for the two-site polaron) neighboring O atoms, among twelve closest to the K vacancy, has been allowed

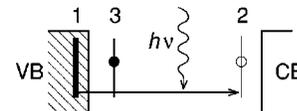


FIG. 3. Sketch of the polaron optical transition from the quasiloocal state 1 near the top of the valence band to the hole state 2 below the conduction band bottom. 3 indicates the level of an unpaired electron.

TABLE I. Absorption ( $E_{\text{abs}}$ ) and lattice relaxation ( $E_{\text{rel}}$ , relative to the perfect crystal with a K vacancy) energies (eV), calculated by LMTO and INDO methods.

Energy method	$E_{\text{abs}}$		$E_{\text{rel}}$	
	INDO	LMTO	LMTO	INDO
Uniform breathing			0.01	0.08
One-site polaron	0.90		0.12	0.40
Two-site polaron	0.95		0.18	0.53

for, and the changes in the total energy (as compared to the unrelaxed perovskite structure with a K atom removed) have been analyzed. Also, we studied the fully symmetric relaxation pattern (breathing of twelve O atoms) around the vacancy. Different relaxation patterns considered in the present study are shown in Fig. 1. The positions of more distant atoms in the supercell were kept fixed.

### III. RESULTS

The removal from the supercell of a K atom with its 7 electrons contributing to the valence band (VB) produces slightly different effects on the electronic structure, as described within the DFT and the HF formalism. According to the LMTO result, the Fermi energy lowers, and the system becomes metallic (remaining nonmagnetic). Therefore, no specific *occupied* localized state is associated with the vacancy. The local density of states (DOS) at the sites of interest is shown in Fig. 2. As is typical for LDA calculations, the one-electron band gap in  $\text{KNbO}_3$  comes out underestimated ( $\approx 2$  eV) as compared to the experimental optical gap ( $\approx 3.3$  eV). The removal of a K  $4s$  electron amounts to adding a hole which forms a localized state at  $\approx 10$  eV above the Fermi level, i.e., above the unoccupied Nb  $4d$  band. In the  $2p$  DOS of O atoms neighboring the vacancy, a quasilocal state (that effectively screens the hole) is visible just below the Fermi level. Apart from that, the  $\text{O}2p$  DOS is largely unaffected by the presence of the vacancy, and the changes in the DOS of more distant sites (K, Nb) are negligible as compared with those in the perfect crystal. As the cubic symmetry is lifted by allowing a nonuniform relaxation of O atoms, the “screening” quasilocal state is clearly localized at the atom closest to the vacancy. At the same time, the hole state becomes smeared out in energy. This amounts to the bonding being established between the hole and the screening charge on one of its neighbors.

In the INDO treatment, the one-electron optical gap is overestimated, as is typical for the HF calculations ( $\approx 6$  eV, see Ref. 30), but the gap calculated as a difference of total energies in relaxed ground state and excited states ( $\Delta\text{SCF}$  gap) gives for the triplet state 2.9 eV, close to the experiment. The quasilocal “screening” state is described by a wide band close to the VB top. This is consistent with the LDA description. But the INDO calculation also suggests, and this differs from the LDA, that the removal of an electron leaves an unpaired electron state split off at  $\approx 1$  eV above the VB band top. In case of asymmetrical O relaxation, the molecular orbital associated with this state is centered at the displaced O atom, being a combination of the  $2p_x$ ,  $2p_y$  functions of the latter in the setting where the

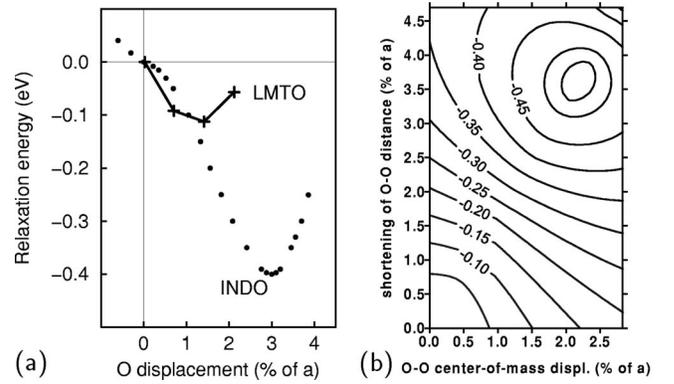


FIG. 4. Relaxation energy for one-site polaron according to LMTO and INDO calculations vs the displacement of one oxygen atom towards the vacancy (a); relaxation energy (eV) for two-site polaron as a function of the center-of-mass displacement of the O-O pair and of the O-O distance according to the INDO calculation (b).

plane spanned by their lobes passes through the vacancy site. The same applies qualitatively to the two-site polaron, with the only difference being that the localized state is formed from the  $2p$  orbitals of *both* O atoms approaching the vacancy, with a corresponding symmetry lowering. The localized hole state is also present in the HF description but lies much lower than the corresponding state in the LDA, forming a 0.9-eV-wide band located  $\approx 0.2$  eV below the conduction band bottom (see Fig. 3).

Differently from the DFT-based approaches which address in principle only the ground-state electron density, the HF method provides a possibility to evaluate excitation energies by means of the  $\Delta\text{SCF}$  formalism. In agreement with Schirmer’s theory for the small-radius polarons in ionic solids,<sup>31</sup> the optical absorption corresponds to a hole transfer to the state delocalized over nearest oxygens. The absorption energies due to the electron transition from the quasilocal states near the VB top (1, Fig. 3) into the vacant polaron band (2, Fig. 3) for one-site and two-site polarons are close (Table I), and both are two times smaller than the experimental value for a hole polaron trapped by the Ti impurity.<sup>11</sup> This shows that the optical absorption energy of small bound polarons can be strongly dependent on the defect involved. Another important observation is that the  $\Delta\text{SCF}$  energy for absorption turns out to be considerably smaller than the estimate based on the difference of one-electron energies.

In spite of a generally observed considerable degree of covalency in  $\text{KNbO}_3$  and contrary to a delocalized character of the  $F$  center state,<sup>8,9</sup> the one-site polaron state remains well localized at the displaced O atom, with only a small contribution from atomic orbitals of other O ions but none from K or Nb ions. Although there are some differences in the description of the (one-particle) electronic structure within the DFT- and HF-based methods, the trends in the total energy driving the structure optimization remain essentially the same. In both approaches, both one-site and two-site configurations of the hole polaron are much more energetically favorable than the fully symmetric (breathing mode) relaxation of twelve O atoms around the K vacancy. This is in line with what is known about small-radius polarons in other ionic solids<sup>13,31</sup> and is caused by the fact that the lattice polarization induced by a point charge is much

larger than that due to a delocalized charge.

In the case of the one-site polaron, a single  $O^-$  ion is displaced towards the K vacancy by 1.5% of the lattice constant (LMTO) or by 3% (INDO)—see Fig. 4. The INDO calculations show that, simultaneously, 11 other nearest oxygens surrounding the vacancy tend to be slightly displaced outwards the vacancy. In the two-site (molecular) configuration, a hole is shared by the two O atoms which approach each other—by 0.5% (LMTO) or 3.5% (INDO)—and both shift towards a vacancy—by 1.1% (LMTO) or 2.2% (INDO). The lattice relaxation energies (which could be associated with the experimentally measurable hole thermal ionization energies) are presented in Table I. In both methods the two-site configuration of a polaron is lower in energy.

A comparison of the present, 320-atomic INDO calculation with a preliminary calculation<sup>29</sup> using 40-atomic LUC and self-consistency in the  $\Gamma$  point of the BZ only shows that the optical absorption energies are not changed considerably, unlike the lattice relaxation energies. The latter now are much smaller and thus in better agreement with the LMTO calculation.

#### IV. CONCLUSIONS

In this pilot study we focused on the quantitative models of hole polarons in  $KNbO_3$ . The main conclusion is that both one-center and two-center configurations are energetically favorable and close in energy (with a slight preference for the two-center configuration), as follows from the numerical

simulation results of two different theoretical methods. The calculated optical absorption energies and the spatial distribution of relevant electronic states could provide guidelines for more direct experimental identification of the defects in question. The calculated hole polaron absorption ( $\approx 1$  eV) is close to the observed short-lived absorption band energy;<sup>10</sup> hence this band could indeed arise due to a hole polaron bound to a cation vacancy. Further detailed study is needed to clarify whether such hole polarons are responsible for the effect of the blue-light-induced infrared absorption reducing the second-harmonic generation efficiency in  $KNbO_3$ .<sup>3</sup>

As compared with the DFT results, the INDO (as is generally typical for the HF-based methods) systematically gives larger atomic displacements and relaxation energies. The DFT results are more reliable in what regards the ground state of polarons, whereas the use of the HF formalism was crucial for the calculation of their optical absorption and hence possible experimental identification.

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