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## Semi-Empirical Calculations of Hole Polarons in MgO and KNbO<sub>3</sub> Crystals

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The semi-empirical quantum chemical INDO method has been used for cluster and large unit cell calculations of hole polarons bound to a cation vacancy in highly ionic MgO and partly covalent perovskite KNbO<sub>3</sub>. In both cases a hole is well localized on an oxygen atom displaced towards the vacancy. The calculated optical and thermal ionization energies for V<sup>-</sup> and V<sup>0</sup> centers are in excellent agreement with experimental data for MgO. In KNbO<sub>3</sub> we predict the existence of one-site and two-site (molecular) polarons with close absorption energies ( $\approx 1$  eV). The relevant experimental data are discussed.

### 1. Introduction

Oxide crystals have numerous technological applications. In particular, ionic MgO is one of the basic ceramic materials, whereas partly covalent KNbO<sub>3</sub> is used in nonlinear optics and holography. Properties of both, quite different, oxide crystals are affected by point defects unavoidably present in real materials. One of the most common defects is an intrinsic cation vacancy. In irradiated MgO the latter is known to trap one or two holes giving rise to V<sup>-</sup> and V<sup>0</sup> centers [1, 2] which are nothing but *bound hole polaron and bipolaron*, respectively. In the V<sup>-</sup> center a hole is trapped by one of the O<sup>2-</sup> ions neighbouring to the cation vacancy, thus creating an O<sup>-</sup> 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 ( $S = 0$ ) [3] and slightly perturbed absorption band. For more detailed discussion of the optical and ESR properties of these defects, see the review article [1].

Several theoretical studies were performed to understand properties of V<sup>-</sup> centers in MgO. In pioneering papers [4, 5] published in the middle of the 70ies it was shown that the observed 2.3 eV band corresponds to a *small-polaron (charge transfer) transition* of a hole from O<sup>-</sup> to the equatorial O<sup>2-</sup> neighbouring ions, at a frozen lattice configuration – a model suggested for the first time by Schirmer et al. [6]. The key factor in a hole localization on a single O<sup>2-</sup> ion lies in the asymmetric displacement of one of six (otherwise equivalent) oxygen atoms from a regular lattice site. This displacement was calculated in [4, 5, 7] using a shell model as implemented into the HADES code. These calculations have, however, several limitations: (i) assumption that a hole is entirely localized by a single oxygen ion; (ii) the short-range interaction between O<sup>-</sup> and sur-

rounding ions is assumed to be the same as for a regular  $O^{2-}$  ion; (iii) quantum mechanical treatment of a single  $O^-$  ion does not allow to study directly the small-polaron transition of a hole to nearest  $O^{2-}$  ions.

These limitations could be avoided by using larger quantum clusters with self-consistent treatment of the electronic/atomic structure and hole density distribution. A good example is the recent *ab initio* SCF scattered wave calculation [8] for a crystalline cluster of seven atoms which predicted the existence of two more absorption bands for the  $V^-$  center – at 2.9 and 4.7 eV. However, much large clusters are needed for a correct study of excited states and the  $V^0$  center containing two holes. For this purpose semi-empirical quantum chemical methods are well suited. The first successful attempt of this kind has been done long ago, in the 70ies, for a 27-atom cluster using the Mulliken-Ruedenberg scheme [9]. Since then no systematic quantum chemical studies were performed for the  $V^-$  and  $V^0$  centers in MgO.

Similarly, very little is done so far in understanding hole polarons in perovskite  $KNbO_3$ . Ti doped  $KNbO_3$  shows an ESR signal which was interpreted as likely due to the two-site polaron next to the impurity [10]. The relevant absorption band lies at 2 eV. Transient optical absorption spectra induced by a pulsed electron beam reveal several bands, one of them is at 1.2 eV [11]. Probably, this is caused by the  $O^-$  bound polaron. No polarons associated with the K vacancy were detected yet in this material but similarly to MgO we expect such defects to exist. For example, in  $BaTiO_3$  hole polarons were found which are bound to Na and K alkali ions replacing Ba and thus forming a negatively charged site attracting a hole [12]. As to theoretical studies of defects in  $KNbO_3$ , at present they include mainly vacancy formation energies calculated by a shell model [13] and the electronic F-type center (O vacancy with trapped electron) quantum mechanical calculations [14, 15]. Due to considerable covalency of the chemical bonding in perovskites, it is not clear *a priori* how strongly a hole is localized on a single oxygen ion, as well as how many surrounding atoms are displaced.

Therefore, in this paper we perform hole polaron simulations in both cubic crystals – MgO and  $KNbO_3$  – using quantum chemical calculations for big clusters.

## 2. Method

The semi-empirical, quantum chemical method of the Intermediate Neglect of the Differential Overlap (INDO) [16] has been used in this study since it demonstrated very good results in previous calculations of defects in many oxides including MgO [17, 18] and  $KNbO_3$  [14, 19]. This method is based on the Hartree-Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defective crystals. The more so, it permits easy calculations for a cluster embedded into the electrostatic field of the rest of the crystal and for periodic systems, using e.g. the large unit cell (LUC) model. In the present polaron simulations, a cation is removed from the center of a cluster or LUC, the number of electrons is reduced by one (that is, a hole is inserted), and the total energy is minimized with respect to the displacements of the surrounding atoms making no *a priori* assumptions about an electron (hole) density distribution.

In MgO calculations were done for 125-atom clusters, the basis set is the same as in previous MgO studies [17, 18]. This cluster has  $O_h$  symmetry and a cubic shape. It simulates nine spheres of atoms around a cation vacancy. Before inserting a defect into

a cluster, cluster atoms were allowed to relax to the minimum of the total energy. We found this relaxation to be very small even for boundary atoms, which demonstrates that the electrostatic field of the rest of the crystal is a good boundary condition for a highly ionic MgO.

To avoid a boundary condition problem for a cluster in partly covalent KNbO<sub>3</sub>, the 40-atom LUC was used which is a  $2 \times 2 \times 2$  extension of the primitive unit cell of five atoms. That is, we have in KNbO<sub>3</sub> a periodic array of defects with a period of  $2a_0$  (the lattice constant in KNbO<sub>3</sub>,  $a_0 = 4.016 \text{ \AA}$ ). Our experience with a larger,  $3 \times 3 \times 3$  LUC used for the F-center calculations [14] has demonstrated that the 40-atom LUC is sufficiently large for localized defects in KNbO<sub>3</sub> and permits to avoid considerable interaction between periodic defects.

The relevant detailed analysis of the INDO parameterization is given in [19]. Note here only that the INDO reproduces surprisingly well results of an *ab initio* study of its electronic structure, including the equilibrium ground state for several ferroelectric phases, as well as  $\Gamma$  phonon frequencies. In this paper, we restrict ourselves to the cubic phase of KNbO<sub>3</sub>. The optical absorption energies are calculated using the standard  $\Delta$  SCF procedure.

### 3. Results and Discussion

#### 3.1 MgO

The optimized geometry of the  $V^-$  center (Fig. 1a) 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 ( $2.1 \text{ \AA}$ ). The displacements of other atoms are insignificant. The effective charges of the ions in a perfect crystal ( $\pm 1.85 e$ ) 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 [6]. The calculated optical absorption energy of 2.2 eV is close to the experimental value (Table 1).

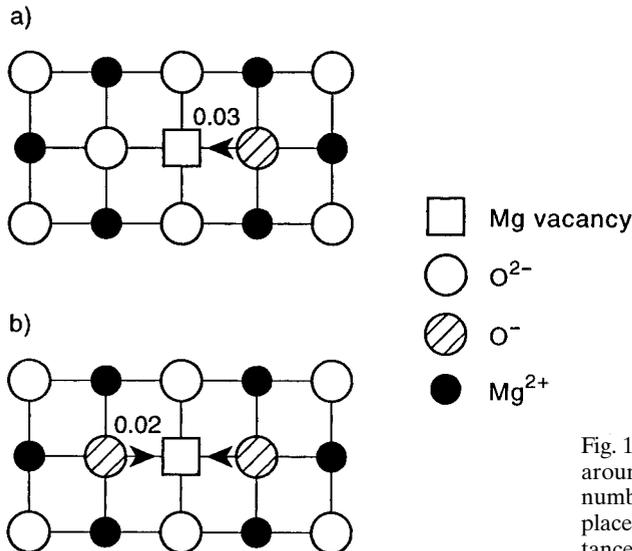


Fig. 1. A fragment of the MgO lattice around the a)  $V^-$  and b)  $V^0$  centers. The numbers show the calculated  $O^-$  ion displacements (in units of the Mg–O distance)

Table 1

Absorption ( $E_{\text{abs}}$ ) and thermal ionization ( $E_{\text{th}}$ ) energies calculated for the hole centers. The experimental data [1, 2] are given in parentheses

energy (eV)	MgO	KNbO <sub>3</sub>
$E_{\text{abs}}$	2.20 (2.3) <sup>a)</sup>	0.95 <sup>c)</sup>
	2.18 (2.3) <sup>b)</sup>	0.98 <sup>d)</sup>
$E_{\text{th}}$	1.6 (1.40) <sup>a)</sup>	1.22 <sup>c)</sup>
	0.8 (0.95) <sup>b)</sup>	1.74 <sup>d)</sup>

<sup>a)</sup> V<sup>-</sup> centre (one-site polaron); <sup>b)</sup> V<sup>0</sup> centre (bipolaron); <sup>c)</sup> one-site polaron; <sup>d)</sup> two-site (molecular) polaron

The thermal ionization energy necessary to release a hole to the valence band is found to be 1.6 eV. The study of the ESR properties is now in progress.

For the V<sup>0</sup> center shown in Fig. 1b, we have found that the minimum energy corresponds to the two holes sitting on the opposite sides of the Mg vacancy, in agreement with experiment, which is accompanied by 2% displacement of the two relevant O<sup>-</sup> ions. The calculated absorption energy is close to that for the V<sup>-</sup> center and experiment (Table 1). An even more encouraging fact is a good agreement between the calculated thermal ionization energy (0.8 eV) of a second hole and its experimental value.

### 3.2 KNbO<sub>3</sub>

We found *two* energetically favourable atomic configurations in which a hole is well localized: a sketch of the relevant one-site and two-site polarons is presented in Fig. 2. In the former case the O<sup>-</sup> ion is displaced towards the K vacancy by 5% (in units of the lattice constant  $a_0$ ). Simultaneously, eleven other oxygen atoms surrounding the vacancy are displaced outwards by  $\geq 1\%$  only. The thermal ionization energy is found to be 1.22 eV. Probably, this is related to the measured activation energy of 1.4 eV for a hole polaron motion reported in [20].

Previous calculations [19] have shown that in pure KNbO<sub>3</sub> the static effective charges of atoms differ strongly from the ionic charges: 0.543  $e$  for K, 2.02  $e$  for Nb and  $-0.854 e$  for O, respectively. This is caused primarily by a high covalency of the Nb–O bonds. However, despite this fact, in a 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. This is in contrast with properties of electronic F-type centers where the ground state contains mainly the contribution from Nb atoms next to the O vacancy [14, 15]. In agreement with Schirmer’s polaronic model, the optical absorption (Table 1) corresponds to a hole transfer to the state delocalized over nearest oxygen atoms.

In the two-site (molecular) polaron the two oxygen atoms sharing a hole approach each other by 13% of the distance in a perfect lattice, i.e., to within 2.45 Å. Simultaneously, its center of mass is displaced towards the K vacancy by 4%  $a_0$ . The other ten nearest O ions are displaced outwards the K vacancy, like in the one-site hole case. The calculated absorption energy is quite close to that for the one-site polaron (Table 1) but twice smaller than the experimental value for a hole polaron trapped near Ti [10]. This

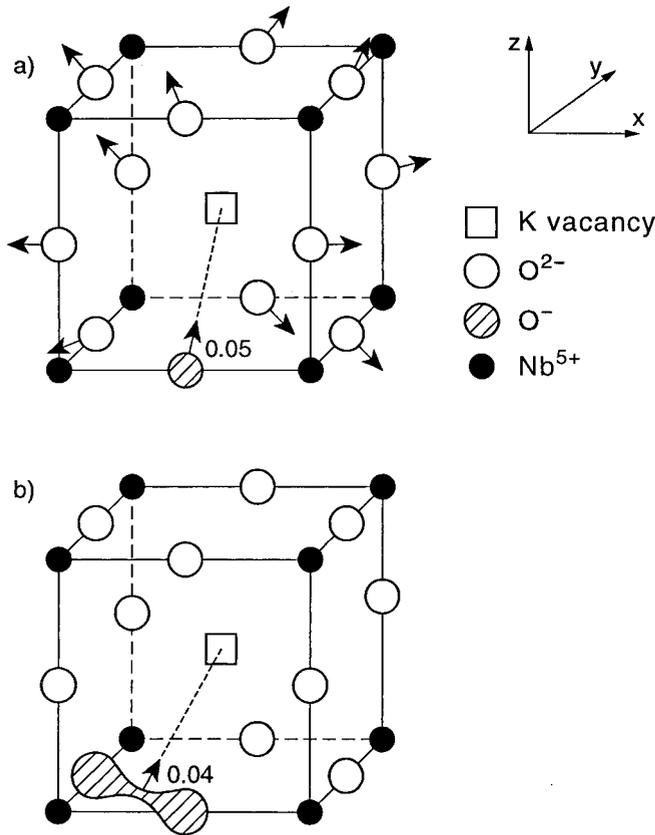


Fig. 2. Same as in Fig. 1 for a) one-site and b) two-site hole polarons in KNbO<sub>3</sub>. Note that in a) the magnitudes of eleven O<sup>2-</sup> ion displacements and that for the O<sup>-</sup> are exaggerated: in fact, the former are smaller by a factor about four. In b) O<sup>2-</sup> displacements are not shown at all since they are qualitatively similar to those in a)

shows that the optical absorption energy of small bound polarons could be strongly dependent on the defect involved.

#### 4. Conclusions

(i) Due to a net charge neutrality of bound hole polarons in both MgO and KNbO<sub>3</sub> the relaxation of only surrounding ions is considerable which justifies the use of smaller clusters (30-40 atoms) in future calculations.

(ii) Further detailed study is needed to clarify whether the hole polaron absorption of  $\approx 1$  eV predicted here for KNbO<sub>3</sub> is related to the short-lived absorption band at 1.2 eV observed in [11] and/or if hole polarons are involved in the effect of the blue light-induced infrared absorption (BLIIRA) reducing the second-harmonic generation efficiency in KNbO<sub>3</sub>.

(iii) Of great interest are detailed *ab initio* polaron simulations which would include the electron correlation effects (cf. [21]). This could give more confidence to the pre-

sent results and would permit more precise comparison of the relative energy gain for the one- and two-site polarons which determines their possible coexistence.

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