COMPUTER SIMULATIONS OF DEFECTS IN PEROVSKITE KNbO₃ CRYSTALS

R. I. EGLITISᵃᵇ, E. A. KOTOMINᵇᶜ, A. V. POSTNIKOVᶜ, N. E. CHRISTENSENd, M. A. KOROTInᵉ, and G. BORSTELᶜ

ᵃInstitute of Materials Research & Engineering, National University of Singapore, Singapore 119260;ᵇInstitute of Solid State Physics, University of Latvia, 8 Kengaraga, Riga LV-1063, Latvia;ᶜUniversität Osnabrück – Fachbereich Physik, Osnabrück D-49069, Germany;ᵈInstitute of Physics and Astronomy, University of Aarhus, Aarhus C, DK-8000, Denmark;ᵉInstitute of Metal Physics, Yekaterinburg GSP-170, Russia

An *ab initio* LMTO approach and semi-empirical quantum chemical INDO method have been used for supercell calculations of basic point defects – *F*'-type centers and hole polarons bound to cation vacancy – in partly covalent perovskite KNbO₃. We predict the existence of both one-site and two-site (molecular) polarons with close absorption energies (∼1 eV). The relevant experimental data are discussed and interpreted.

**Keywords**: ferroelectrics, atomic and electronic structure, vacancies, polarons, *ab initio* and semi-empirical methods

INTRODUCTION

Perovskite KNbO₃ crystals are widely used in non-linear optics and holography. Their properties are influenced by point defects, primarily by vacancies. Relatively little is known about such intrinsic point defects in KNbO₃. A broad absorption band around 2.7 eV has been observed in electron-irradiated crystals and ascribed to the *F*-type centers (O vacancy which trapped one or two electrons – *F*⁺ and *F* centers, respectively). Transient optical absorption at 1.2 eV has been associated recently in analogy with other perovskites, with a hole polaron (a hole bound to some defect). The ESR study of KNbO₃ doped with Ti⁴⁺ gives a proof that holes could be trapped by such negatively charged defects. For example, in BaTiO₃, hole polarons were also found which are bound to Na and K alkali ions replacing...
Ba and thus forming a negatively charged site attracting a hole. Primary candidates for such defects are cation vacancies. In irradiated MgO they are known to trap one or two holes giving rise to the $V^{-}$ and $V^{0}$ centers which are nothing but \textit{bound hole polaron and bipolaron}, respectively. Some preliminary theoretical study has been already done by us on $F$ centers in KNbO$_{3}$ and on hole polarons in this material. In the present paper, we report the results of additional computer simulations using the same two different approaches as e.g. in Ref. \cite{7}. We restrict ourselves to the cubic phase of KNbO$_{3}$, with the lattice constant $a_0=4.016\ \text{\AA}$.

\section*{METHODS}

For the study of the ground-state atomic and electronic structure we used the \textit{ab initio} linearized muffin-tin orbital (LMTO) method based on the local density approximation (LDA). For structure optimizations, the full-potential version of LMTO by van Schilfgaarde and Methfessel has been used. As an extension of the analysis previously done in Ref. \cite{7} for the $F$ center, we applied the tight-binding LMTO method in the modification incorporating the LDA+$U$ formalism. The latter allows to maintain the orbital dependency of the potential and, to some extent, to treat Coulomb correlation effects within localized shells beyond the LDA. We used this approach for introducing an \textit{ad hoc} upward shift of the conduction band (mostly consisting of Nb $4d$ states) and splitting-off of the $F$ center level from it in a different way than it was done in Ref. \cite{7}. Moreover, this allowed us to analyze the symmetry of the $F$ center wavefunction. We used $U=8$ eV and $J=0$ (for the Nb $4d$ shell) as parameters of the LDA+$U$ method.

In parallel with the LMTO, the semi-empirical method of the Intermediate Neglect of the Differential Overlap (INDO) modified for ionic and partly ionic solids has been used (see Ref. \cite{13} for details of its application to KNbO$_{3}$). Differently from the LMTO, the INDO method is based on the Hartree-Fock formalism and allows self-consistent calculations of the excited states of defects and thus the relevant absorption energies using the
so-called $\Delta$SCF method. The simulation of all defects has been done within a supercell approach, with one (neutral) O atom removed to model the $F$ center and two atoms, O and K, removed to simulate the $F^+$ center. For the modeling of the hole centers, a K atom has been removed, and the actual type of the hole polaron (one-site and two-site) was set by the symmetry of the local lattice relaxation. In LMTO calculations, the $2 \times 2 \times 2$ supercells containing 40 atoms were used in all cases, i.e. with repeated point defects separated by $\sim 8$ Å. Only the positions of nearest neighbors to the defect were relaxed. In the INDO calculations we used much larger, $4 \times 4 \times 4$ supercells (320 atoms), and allowed for the relaxation of more distant neighbors. Besides decreasing the residual interaction between impurities in adjacent supercells, this effectively takes into account the dispersion of energy bands over the Brillouin zone of KNbO$_3$ up to a better extent than it was possible in previous defect calculations\[7, 8\] with smaller supercells.

RESULTS AND DISCUSSIONS

$F$-type centers

In the 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 nondegenerate and a doubly-degenerate levels). The optimized atomic relaxation around the $F$ center as done by the LMTO indicates the outward shift of the Nb neighbors to the O vacancy by $3.5\% a_0$. The associated lattice relaxation energy is shown in Table 1.

The optimized Nb relaxation found in the INDO simulations was $3.9\%$, i.e. very close to the \textit{ab initio} calculations. The outward relaxation of nearest K atoms and inward displacements of O atoms are much smaller. They give $\approx 20\%$ of the net relaxation energy of $1.35$ eV. The $F$ center local energy level lies $\approx 0.6$ 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 $\approx 0.6$ \textit{e} resides at the orbitals centered at the vacancy site; hence the electron localization at the defect is much smaller.
TABLE I  Absorption ($E_{\text{abs}}$) and lattice relaxation ($E_{\text{rel}}$) energies (eV) as calculated for the electron and hole centers by LMTO and INDO methods.

|                  | $E_{\text{abs}}$ |               | $E_{\text{rel}}$ |               |
|------------------|------------------|---------------|------------------|---------------|
|                  | INDO             | LMTO          | INDO             |               |
| $F^{-}\text{-center}$ | 2.68; 2.93       | 0.5           | 1.35             |               |
| $F^{+}\text{-center}$ | 2.30; 2.63       | —             | 2.33             |               |
| one-site polaron  | 0.9              | 0.14          | 0.4              |               |
| two-site polaron  | 0.95             | 0.18          | 0.53             |               |

than is known for $F$ centers in ionic oxides (see Ref. [14] for comparison). The symmetry analysis of the ground-state wave function associated with the $F$ center, done by the TB-LMTO method with the use of the LDA+$U$ formalism and by INDO, revealed the same result, namely that the major contribution comes from the $e_g$ states centered at Nb neighbors (more specifically, it is essentially the $3z^2-r^2$ component, with $z$ in the direction towards the $F$ center). The partial densities of states from the LMTO calculation are shown in Fig. 1.

![FIGURE 1](image-url)  

FIGURE 1  Local density of states of the $F$-center (left panel) and of the Nb atom nearest to it as calculated by the LMTO method.
For the $F^+$ 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: a share of the electron density inside the O vacancy decreases to 0.3 e.

The optical absorption energies calculated by means of the $\Delta$SCF method for the $F^+$ and $F$ centers are given in Table 1. The two absorption bands predicted for the former center are shifted to the low-energy side, which is in agreement with similar defects in ionic oxides. However, both defects are predicted to have one of the bands around 2.6–2.7 eV, in agreement with the experimental observation.

**Hole Polarons**

Both *ab initio* and semi–empirical calculations agree that there are two energetically favorable atomic configurations in which a hole is well localized: one-site and two-site (molecular) polarons. In the former case, a single O$^-$ ion is displaced towards the K vacancy by 1.5 % (LMTO) or 3% (INDO). The INDO calculations show that simultaneously, 11 other nearest oxygens surrounding the vacancy are 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 2.5% (INDO). The lattice relaxation energies (which could be associated with the experimentally measurable hole thermal ionization energies) are presented in Table 1. In both methods the two-site configuration of a polaron is lower in energy.

In spite of general observation of a considerable degree of covalency in KNbO$_3$ (see, e.g., Ref. [13] for a discussion) and contrary to a delocalized character of the $F$ center state, 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 not K or Nb ions. In agreement with Schirmer’s theory for the small-radius polarons in ionic solids, the optical absorption corresponds to a hole transfer to the state delocalized over nearest oxygens. The calculated absorption energies for one-site and two-site polarons are
close (Table 1) and twice smaller than the experimental value for a hole polaron trapped near Ti. This shows that the optical absorption energy of small bound polarons could be strongly dependent on the defect involved.

CONCLUSIONS

(i) The two different methods used for defect calculations reveal a qualitative agreement, despite the fact that the INDO (as is generally typical for the Hartree-Fock-based schemes) systematically gives larger atomic displacements and relaxation energies. Both two–electron F-center calculations demonstrate a strong electron delocalization from the O vacancy over the two nearest Nb atoms; very likely due to a considerable covalency of the chemical bonding in KNbO$_3$, and predict the $e_g$ symmetry of the wave function which could be checked experimentally. Both methods agree also that both one–site and two–site hole polarons bound to the cation vacancy are energetically favorable, with a preference to the latter.

(ii) The INDO calculations of the optical absorption energies strongly support the interpretation of the experimentally observed band at 2.7 eV as due to the $F$-type centers. To distinguish between the $F$ and $F^+$ centers, the ESR measurements should be used.

(iii) The calculated hole polaron absorption ($\approx$1 eV) is close to the observed short-lived absorption band energy and thus could arise due to a hole polaron bound at cation vacancy. Further detailed study is needed to clarify whether such hole polarons are responsible for the effect of the blue-light-induced-infrared-absorption (BLIIRA) reducing the second-harmonic generation efficiency in KNbO$_3$.

Acknowledgments
This study was partly supported by the DFG (a grant to E. K.; the participation of A. P. and G. B. in the SFB 225), Volkswagen Foundation (grant to R. E.), and the Latvian National Program on New Materials for Micro- and Optoelectronics (E. K.). M. K. appreciates the hospitality of the University
of Osnabrück during his stay there. Authors are greatly indebted to Prof. M. R. Philpott for valuable discussions.

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