QUANTUM MECHANICAL MODELLING OF PURE AND DEFECTIVE KNbO₃ PEROVSKITES

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Abstract. Ab initio electronic structure calculations using the density-functional theory (DFT) are performed for KNbO₃ with and without defects. Ferroelectric distortive transitions involve very small changes in energies and are therefore sensitive to DFT-approximations. This is discussed by comparing results obtained with the local density approximation (LDA) to those where generalized gradient approximations (GGA) are used. The results of ab initio calculations for F-type centers and bound hole polarons are compared to those obtained by a semiempirical method of the Intermediate Neglect of the Differential Overlap (INDO), based on the Hartree–Fock formalism. Supercells with 40 and 320 atoms were used in these two approaches, respectively. The relevant experimental data are discussed.
1. Introduction

KNbO$_3$ is one of the oldest known room-temperature ferroelectric materials, that undergoes a sequence of ferroelectric transitions from the high-temperature cubic perovskite structure [1]. The simplicity of crystal structure makes it appealing for \textit{ab initio} theory simulations, whereas interesting photorefractive characteristics and low cost keep KNbO$_3$ in a list of serious candidates for practical applications in electro-optical devices even with the advent of new ferroelectric substances. From the point of view of applications, KNbO$_3$ always contains defects – either intentionally introduced ones (like substitutional impurities introduced in the search for particular optical characteristics), or those immanently present even in nominally pure samples (vacancies on different sublattices). In the latter case, the identification of defects accounting for (sometimes undesirable) absorption bands may present a problem.

The \textit{ab initio} microscopic simulations of electronic structure, lattice distortions and related optical excitations in the presence of defects may meet the practical needs of defects’ identification quite efficiently. However, the theory faces certain problems already in the description of ideal defect-free KNbO$_3$. For one thing, a small magnitude of atomic displacements and correspondingly small (of the order of 1 mRy per formula unit) energy gains related to ferroelectric transition set the standards of accuracy for an underlying calculation quite high. The experience of precision total-energy calculations based on the local density approximation (LDA) within the density functional theory (DFT) have shown that the equilibrium volume, although only slightly (by $\approx 5\%$) underestimated with respect to the experimental one, is nevertheless almost too small for the ferroelectric instability to become qualitatively possible [2]. This problem may be solved on the path of constructing better approximations for the exchange-correlation energy within the DFT than the LDA. When turning to the simulations of electronic excitations in defect systems, the DFT-based methods are not always fully satisfactory. As a simple alternative, the Hartree-Fock schemes may prove to be useful.

In the present paper, we summarize essential results of our recent studies devoted to different aspects of \textit{ab initio} electronic structure simulations in perovskites. We addressed the problem of tuning the generalized gradient approximation (GGA) for KNbO$_3$, among other perovskites, in Ref. [3]. Two different vacancy-type defects, namely $F$-centers associated with an O vacancy, and hole polarons, bound assumedly on a K vacancy, have been studied respectively in Refs. [4] and [5]. In the following, we briefly discuss the technical side of the calculations and concentrate on three above-mentioned problems, refering to related experimental information.
2. Methods

Our *ab initio* DFT calculations in all three cases used linear band structure methods [6], the full-potential linear augmented-plane-wave (FLAPW) method [7] for pure KNbO$_3$ and the linear muffin-tin orbital (LMTO) scheme, also in a full-potential implementation [8], for the study of defects (in the supercell approach). The $2 \times 2 \times 2$ supercells were chosen, i.e. the distance between repeated point defects was $\approx 8$ Å. As a consequence of the large number of eigenstates per $k$-point in a reduced Brillouin zone (BZ) of the supercell and of the metallicity of the doped system, it was essential to maintain a dense mesh for the $k$-integration by the tetrahedron method over the BZ. Specifically, clear trends in the total energy as function of atomic displacements were only established at $\frac{1}{16}$ divisions of the BZ (i.e., 186 irreducible $k$-points for a one-site polaron).

In the study on pure KNbO$_3$, we concentrated on the accuracy of total energy evaluations obtained with different approximation schemes in the DFT. The LDA in general leads to overbinding when applied to solids, and this error is particularly serious for perovskites where predictions of ferroelectric properties are incorrect if calculated at too small volumes. A simple way to improve accuracy simply consists in performing the calculations for the experimental volume, but this still leaves the question open about additional “LDA errors”. Some improvement over the LDA has been obtained by using gradient approximations for better descriptions of the inhomogeneous electron gas. In the Kohn-Sham density functional theory only the exchange-correlation energy $E_{XC} = E_X + E_C$ which is a functional of the electron spin densities must be approximated, and for slowly varying densities, $n$, it can be expressed as the volume integrals of $n$ times $\epsilon_{xc}^{uni\mu f}$ in the LDA case and $f(n_1, n_2, \nabla n_1, \nabla n_2)$ for the GGA case. For practical calculations the exchange-correlation energy density of a uniform electron gas, $\epsilon_{xc}^{uni}$ ($n_1, n_2$), and $f$ must be parametrized. The form of $\epsilon_{xc}^{uni\mu f}$ is now well established but which is the best choice of $f$ is still under debate.

The GGA version suggested by Perdew, Burke and Ernzerhof (PBE) [9] has been very useful in several cases, but some uncertainty in its use is related to the choice of the parameter $\kappa$, in the enhancement factor $F_X(s)$ which is directly associated to the degree of localization of the exchange-correlation hole. (Here the variable $s$ is a measure of the relative density gradient, $s = |\nabla n|/2k_F n$, $k_F$ giving the Fermi wavenumber of an electron gas of density $n$). In their original work PBE proposed $F_X(s) = 1 + \kappa - \kappa/(1+\mu s^2/\kappa)$ which satisfied the inequality $F_X \leq 1.804$ with $\kappa = 0.804$ and with the value of $\mu \approx 0.21951$. Zhang and Yang found [10] that the results for several atoms and molecules were improved by increasing $\kappa$ beyond the originally proposed value of 0.804. But, this does not hold for all types of

bonds [11], and it may well happen that applications to solids appear to be improved when smaller values of $\kappa$ are used. The parameter $\kappa$ might be a weak function of the reduced Laplacian, $\kappa = g[\nabla^2 n/(2k_F)^2 n]$.

The motivation for using the DFT-based and Hartree-Fock (HF) -based calculation methods in parallel, when applied to defects, is to combine strong sides of both in a single study. The DFT is expected to be able to provide 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 omission of correlation effects. On the other hand, the HF formalism is well 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. This 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 [12]. For a HF calculation scheme in a present study, the semi-empirical Intermediate Neglect of the Differential Overlap (INDO) [13] method, modified for ionic and partly ionic solids [14, 15], has been used. The supercells of the same size as with the FP-LMTO method, i.e. $2 \times 2 \times 2$, were used for the study of $F$ and $F^+$ centers, and a larger supercell, $4 \times 4 \times 4$ (320 atoms), for the more recent calculation of a hole polaron. The effect of the supercell size can be seen from the comparison of the present data (reproduced from Ref. [5]) with those of Ref. [16] where a small 40-at. supercell has been used for the hole polaron as well. In the supercell INDO calculations, the Brillouin zone summation was restricted to the zone center only (in the appropriately reduced zone). This introduced a certain error, especially large for small supercells. A discussion on possible magnitude of such error is given in Ref. [4]. The parametrization of the INDO method for the calculations on KNbO$_3$ has been done in Ref. [17].

3. Pure KNbO$_3$: GGA vs. LDA

The accuracy of the LDA when applied to the perovskites, as well as the effects of introducing the GGA improvements, are illustrated in the following by the calculations of: 1) the energy-volume curves from which lattice parameters and bulk moduli are derived, 2) $\Gamma_{15}$ phonon modes for the cubic structure, and 3) the tendency to undergo a ferroelectric transition when the atoms are displaced according to the soft-mode displacement pattern.

In that connection the sensitivity to the choice of $\kappa$ in the PBE GGA is examined. In Fig. 1 the values of $V/V_0$ ($V_0$ is the corresponding experimental value) are plotted for four perovskites over the range of $\kappa$ values...
Quantum Mechanical Modelling...

![Graph](image)

**Figure 1.** Equilibrium volumes calculated for KNbO$_3$, BaTiO$_3$, SrTiO$_3$ and KTaO$_3$ as functions of the PBE-GGA parameter $\kappa$. ($V_0$ are the experimental equilibrium volumes.

**TABLE 1.** Frequencies of the $\Gamma_{15}$ modes (in cm$^{-1}$), lattice parameter $a$ (in Å) and bulk modulus $B$ (in GPa) in KNbO$_3$ as calculated in the LDA and GGA approximations. $i$ in the frequency values indicate that these are imaginary, i.e. soft mode. Note that all phonon frequencies are calculated at the experimental equilibrium volume. In parantheses: bulk modulus at the experimental equilibrium volume.

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>GGA ($\kappa=0.804$)</th>
<th>GGA ($\kappa=\kappa_{eq}$)</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequencies</td>
<td>211i</td>
<td>197i</td>
<td>195i</td>
<td>soft</td>
</tr>
<tr>
<td></td>
<td>166</td>
<td>182</td>
<td>179</td>
<td>198</td>
</tr>
<tr>
<td></td>
<td>466</td>
<td>478</td>
<td>478</td>
<td>521</td>
</tr>
<tr>
<td>$a$</td>
<td>3.96</td>
<td>4.04</td>
<td>4.016</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>206(155)</td>
<td>171(186)</td>
<td>138</td>
<td></td>
</tr>
</tbody>
</table>

in the PBE-GGA functional varying from 0.3 to 0.804. As can be seen, both BaTiO$_3$ and KNbO$_3$ would give perfect determination of the lattice parameter ($V/V_0=1$) for $\kappa \approx 0.6$. In the case of SrTiO$_3$ and KTaO$_3$ the value should be further reduced to $\kappa \approx 0.4$. The need of varying $\kappa$ from one system to another reflects the fact that the localization of the exchange-correlation hole is system-dependent.

In order to clarify the effect of the GGA functional on the phonon en-
energies, we have performed frozen phonon calculations for KNbO$_3$ at its experimental lattice constant, and examined the effects of choosing different exchange-correlation approximations, i.e. LDA and PBE-GGA with different $\kappa$ values. The calculated frequencies of the $\Gamma_{15}$ modes and the experimental values are shown in Table 1. It is seen that the GGA hardens the phonon frequencies (as compared to the LDA results). This hardening produces a slight reduction of the errors, since the LDA provides phonon frequencies which are underestimated by 10–20% as compared with experiments. The second conclusion concerns the parameter $\kappa$. It is evident from Table 1 that the effect introduced on the GGA phonon frequencies by the modification of $\kappa$ is negligible. In addition, we found [3] that the eigenvectors are practically unchanged.

Finally, to test the sensitivity of the energetics involved in the ferroelectric instabilities when the different exchange-correlation functionals are used, we performed total energy calculations as a function of the off-center displacement of Nb atom. In Fig. 2, we show the energy as a function of such displacement along the (111). Both LDA and GGA (with $\kappa=0.804$ and 0.6) yield a clear ferroelectric instability with similar energetics and displacements, and with an energy gain of $\approx 1.8$ mRy/cell. The similar observation has been done by Singh [18] in his GGA study of KNbO$_3$. 

4. Simulation of defects

It is well understood now that point defects play an important role in the electro-optical and non-linear optical applications of KNbO$_3$ and related ferroelectric materials [1]. The prospects of the use of KNbO$_3$ for the light frequency doubling are seriously affected by the presence of unidentified defects responsible for induced infrared absorption [19]. The photoelectrorefractive effect, important in particular for holographic storage, is also well known to depend on the presence of impurities and defects. Most of as-grown ABO$_3$ perovskite crystals are non-stoichiometric and contain considerable amounts of vacancies.

The electron $F$ and $F^+$ centers (an O vacancy, $V_o$, which traps two or one electron, respectively) [20, 21, 22] belong to the most common defects in oxide crystals. In electron-irradiated KNbO$_3$, a broad absorption band observed around 2.7 eV at room temperature has been tentatively ascribed to the $F$-type centers [23]. These two defects were the subject of recent ab initio LDA and semiempirical calculations [24, 4]. A transient optical absorption band at 1.2 eV has been associated recently [25] in analogy with other perovskites– with a hole polaron (a hole bound, probably, to a K vacancy). The ESR study of KNbO$_3$ doped with Ti$^{4+}$ gives a proof that holes could be trapped by such negatively charged defects [26]. For example, in BaTiO$_3$, the hole polarons bound to Na and K alkali ions replacing Ba and thus forming a negatively charged site attracting a hole [27] have also been found. Cation vacancies are the most likely candidates for binding hole polarons. In irradiated MgO, they are known to trap one or two holes giving rise to the $V^-$ and $V^0$ centers [20, 21] which are in their nature bound hole polaron and bipolaron, 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 quasi-molecule [26, 27, 28].

In the present study, we simulate both electron centers and hole polarons associated with a K vacancy in KNbO$_3$.

4.1. Ф-TYPE CENTERS

In the cubic KNbO$_3$ 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 shows that the Nb neighbours to the O vacancy are displaced outwards by 3.5 $\%$ \(a\). The associated lattice relaxation energy is shown in Table 2.

The optimized Nb relaxation found in the INDO simulations was 3.9 %,
TABLE 2. Absorption ($E_{abs}$) and lattice relaxation energies ($E_{rel}$), for the electron centers and hole polarons (relatively to the perfect crystal with a K vacancy) (in eV), calculated by LMTO and INDO methods.

<table>
<thead>
<tr>
<th></th>
<th>INDO $E_{abs}$</th>
<th>LMTO $E_{rel}$</th>
<th>INDO $E_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$-center</td>
<td>2.68; 2.53</td>
<td>0.5</td>
<td>1.35</td>
</tr>
<tr>
<td>$F^{+}$-center</td>
<td>2.30; 2.63</td>
<td>—</td>
<td>2.33</td>
</tr>
<tr>
<td>one-site polaron</td>
<td>0.9</td>
<td>0.14</td>
<td>0.4</td>
</tr>
<tr>
<td>two-site polaron</td>
<td>0.95</td>
<td>0.18</td>
<td>0.53</td>
</tr>
</tbody>
</table>

*Figure 3.* Local density of states of the $F$-center (left panel) and of the Nb atom nearest to it as calculated by the LMTO method.
i.e. very close to the *ab initio* calculations. The outward relaxation of nearest K atoms and inward displacements of O atoms are much smaller. They contribute ≈20% of the net relaxation energy of 1.35 eV. The F center local energy level lies ≈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 eV resides at the orbitals centered at the vacancy site; hence the electron localization inside vacancy is much weaker than for F centers in ionic oxides where typically 80% of the electron density is localized in the ground state [22]. 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 [29] 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. 3.

For the \( F^+ \) center the relaxation energy of 2.23 eV and the Nb displacements of 5.1% of \( a \) 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 eV. The optical absorption energies calculated by means of the \( \Delta \)SCF method (the difference of total energies in relaxed ground state and excited state) for the \( F^+ \) and \( F \) centers are given in Table 2. Both defects are predicted to have one of the bands around 2.6–2.7 eV, which was observed experimentally [23].

4.2. **HOLE POLARONS**

In the K vacancy-containing supercell, the relaxation of either one (for the one-site polaron) or two neighboring (for the two-site polaron) O atoms, amongst twelve closest to the K vacancy, has been allowed 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.

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 in the HF formalism. According to the LMTO result, the Fermi energy lowers, and the system becomes metallic (remaining non-magnetic). 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. 4. As is typical for LDA calculations, the one-electron band gap in KnBO\(_3\) comes out underestimated (≈2 eV) as compared to the experimental optical gap (≈3.3
Figure 4. Local DOS at the K vacancy site and at the adjacent oxygen atom (top panel) and at Nb and O sites in perfect KNbO$_3$ (bottom panel), as calculated by LMTO.

eV). The removal of a K4s electron amounts to adding a hole which forms a localized state at $\approx 10$ eV above the Fermi level, i.e., above the unoccupied Nb4$d$ band. In the 2$p$-DOS of O atoms neighboring the vacancy, a quasi-local state (that effectively screens the hole) is visible just below the Fermi level. Apart from that, the O2$p$-DOS is largely unaffected by the presence of 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 non-uniform relaxation of O atoms, the “screening” quasi-local 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 case of 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. 6. The INDO calculations show that simultaneously, 11 other nearest oxygens surrounding the vacancy tend to be slightly displaced outswards.
Figure 5. Sketch of the polaron optical transition from the quasi-local 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.

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 2. In both methods the two-site configuration of a polaron is lower in energy.

In the INDO treatment, the one-electron optical gap is overestimated, as is typical for the HF calculations ($\approx 6$ eV [17], but the $\Delta$SCF gap for the triplet state is 2.9 eV, close to the experiment. The quasi-local screening state is described by a wide band close to the VB top. This is consistent with the LDA description. 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, on which about 80% of unpaired spin density is localized. The same applies qualitatively to the two-site polaron, with the only difference 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. 5). In agreement with the general theory of small-radius polarons in ionic solids [28, 30], 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 quasi-local states near the VB top (1, Fig. 5) into the vacant polaron band (2, Fig. 5) for one-site and two-site polarons are close (Table 2), and both are twice smaller than the experimental value for a hole polaron trapped by the Ti impurity [26]. This shows that the optical absorption energy of small bound polarons can be strongly dependent on the defect involved.

In spite of generally observed considerable degree of covalency in KNbO$_3$ and contrary to a delocalized character of the $F$ center state [24, 4], 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 [28, 30] 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.

5. Conclusions

We emphasize that when dealing with tiny (on the energy scale) effects related to the off-center instabilities in ferroelectric perovskites, one should be particularly careful to the details of the method used, like e.g. the treatment of exchange-correlation in a DFT-based $ab$ $initio$ scheme. In the study of charged defects where characteristic energies are much larger, the use of appropriately tuned semiempirical methods may provide reliable results.
Especially for the study of optical excitations, the use of a HF-type scheme in parallel with a DFT-based analysis turns out to be useful.

We demonstrated that the \( F \)-type centers could be responsible for the optical absorption observed around 2.7 eV \[23\]. The calculated polaron absorption (\( \approx 1 \) eV) is close to the observed short-lived absorption band energy \[25\]; hence this band could indeed arise due to a hole polaron bound to a cation vacancy.

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