First-principles calculations for Fe impurities in KNbO$_3$

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Abstract

Nb-substituting Fe impurity in KNbO$_3$ is studied in first-principles supercell calculations by the linear muffin-tin orbital method. Possible ways to account for the impurity charge compensation are discussed. Calculations are done in the local density approximation (LDA) and, for better description of Coulomb correlation effects within the localized impurity states, also in the LDA+$U$ scheme. The achievements and problems encountered in both approaches are analyzed. It is found that the impurity possess either a low-spin configuration (with 0 or 1 compensating electron), or a high-spin configuration (with 2 or 3 compensating electrons), the latter two apparently corresponding to practically relevant rechargeable impurity states.

Keywords: Ferroelectricity, doping, photorefractive effect.

I. INTRODUCTION

Impurities in ferroelectric crystals play an important rôle in many physical applications, particularly in what regards optical absorption and the change of dielectric properties under illumination, the so-called photorefractive effects. For a review on this subject see, e.g., Ref. [1]. The explanation of the photorefractive effect is essentially based on the assumption of the existence of several charge state of an impurity, which can be switched by the drift of electrons or holes in the process of illumination. In what regards specifically Fe-doped KNbO$_3$, one can address Ref. [2] for the description of the models available, and Ref. [3] for practical aspects of tuning photorefractive properties. Therefore, much experimental effort has been concentrated on the elucidating the electron configuration of impurities in question, related lattice relaxation, or other defects coming along with the substitutional impurities. Important information of this kind can be extracted from electron paramagnetic resonance measurements. Earlier studies for Fe in KNbO$_3$ [4] established the presence of Fe$^{3+}$ centers without local charge compensation and also of other centers, that were interpreted as Fe$^{3+}$ with local charge compensation, presumably Fe at Nb site with an oxygen vacancy in the nearest neighborhood. The subsequent studies [5] included more detailed comparison of the spectra with the description based on different structure distortion models. It was suggested that the Fe$^{3+}$ ion is displaced by $\sim$0.2Å towards the neighboring O vacancy. There seems to be now general agreement between the experimentalists that Fe preferentially enters the Nb site in KNbO$_3$. The calculations of the energy balance with empirical interaction potential
(see Ref. [8], with the potentials from Ref. [4]) show beyond doubt that the Fe substitution at
the K site is energetically unfavorable. In contrary to this, Ref. [8] claimed that Fe mostly
substitutes K in KNbO$_3$, based on the similarity of angular yield particle-induced X-ray
emission profiles for K and Fe. This similarity however does not seem highly convincing.
One should note that the Fe doping in KTaO$_3$, that is equistructural and equielectronic to
KNbO$_3$, favors another pattern, with higher probability of entering the K site [3].

In the situation when the information on the electronic structure of doped systems is
available from experiment in a rather indirect way, there is a demand for \textit{ab initio} or other
reliable calculations which would provide the energy positions of impurity levels in the
gap and to compare energetically different mechanisms for the charge compensation and
the relaxation pattern around impurity. To out knowledge, just two attempts have been
undertaken in this direction up to now. The result of a shell-model calculation by Exner [3]
for a Fe at Nb site and an oxygen vacancy as its nearest neighbor is that Fe is displaced by
0.38Å \textit{from} the vacancy, i.e., contrary to what was supposed based on the analysis of the
electron spin resonance data [5]. Also, the displacement of four “equatorial” O neighbors
to Fe is 0.19Å \textit{outwards} in the shell-model calculation [3], contrary to the estimated 0.1Å
\textit{inwards} in Ref. [3]. The \textit{ab initio} calculation with the linearized muffin-tin orbital method
(LMTO) in the atomic sphere approximation (ASA) for one Nb-substituting Fe in the 2×2×2
supercell of KNbO$_3$, without any oxygen vacancies [9], has shown that the “breathing”
relaxation of the O$_6$ octahedron is \~{}0.05Å \textit{outwards}. The shell model calculation for the
same geometry (also in Ref. [9]) as well predicts the outward expansion of O$_6$ of comparable
magnitude.

The deficiencies of these previous calculations are that the shell model depends on the
empirical interaction parameters fitted into it, and normally discards the anharmonic effects,
and the LMTO-ASA calculation is normally too crude for reliable estimates of lattice relax-
ation. Moreover, no data on the electronic structure of impurity was published in Ref. [9].
The aim of our present study is to provide this information, concentrating specifically on
the treatment of different charge configurations within the localized d-shell. In particular,
we compare the treatment within the local density approximation (LDA) with the so-called
LDA+$U$ approach. The calculations are done by a LMTO-ASA method for undistorted
lattice, without introducing oxygen vacancies. The accurate analysis of lattice relaxation,
with and without vacancies, needs the use of a full-potential (FP, i.e., with the potential of
general shape). Such FP-LMTO calculations are in progress and will be reported elsewhere.

\section*{II. CALCULATION METHOD AND SETUP}

The calculations have been done with the LMTO-ASA method [10], in part using the TB-
LMTO code of the O. K. Andersen group in Stuttgart [11]. The LDA+$U$ calculation scheme
(discussed below) has been implemented in another LMTO-ASA code by V. I. Anisimov.
In all calculations, we considered the cubic high-temperature phase of KNbO$_3$ with lattice
constant 4.015Å; atomic sphere radii were 1.639Å for Fe and Nb, 1.964Å for K and 1.050Å
for O. Such choice of radii produces the band structure in reasonable agreement with that
from FP-LMTO calculations [12]. According to our experience, the use of additional empty
spheres in the interstitials of the perovskite structure does not bring any improvement in
the LMTO-ASA calculation. In order to account for the lifting of orbital degeneracy at the Fe site, the minimal point group symmetry, including only inversion, was assumed in the calculations.

Although KNbO$_3$ is not a typically ionic compound, and, moreover, the covalency of the Nb–O bond is quite important for giving rise to ferroelectric instability, it is useful to refer to nominal ionic charges in order to understand why the problem of charge compensation occurs, when one considers the Fe impurity. Fe is either Fe$^{2+}$ or Fe$^{3+}$ in oxides; the substitution of (nominally) Nb$^{5+}$ with Fe$^{3+}$ leaves 2 extra electrons in the system, which can be removed along with one O$^{2-}$ ion, thus restoring the neutrality. This is one possible mechanism of local charge compensation; another, in principle, possible one is that two Fe$^{3+}$ substitute Nb$^{5+}$ and K$^+$. In terms of neutral atoms building the crystal, 30 electrons are provided in total in the valence band per unit cell of KNbO$_3$ (including K3$p$, which are treated as valence band states). If Fe atom with its 8 electrons substitutes Nb, only 5 electrons can be absorbed by the valence band, leaving Fe nominally in the 3$d^3$ configuration. This is possible, but expectedly highly unstable. In order to restore a typical for Fe 3$d^5$ or 3$d^6$ configuration, one should either provide extra electrons, or remove one oxygen atom, thus reducing the capacity of the valence band. There are essentially only two ways to account for a charge compensation in the calculation – one either specifies explicitly the configuration of impurities/vacancies that provides such compensation, or adds extra electrons to the system, implying that their donors are in some distant parts of crystal and do not affect the local electronic structure. The second way is probably technically easier, because one needs only to search for the Fermi energy corresponding to the specified number of extra electrons in each iteration. In order to keep the supercell neutral, a compensating positive charge is added in the background.

Our initial calculations did not consider the charge compensation in any way, simply treating the neutral supercell with one Nb atom substituted with Fe. As a smallest possible supercell for the modeling of isolated impurity, we considered the perovskite cell doubled in all three directions, i.e., including 40 atoms in total. The density of states (DOS) resulting from this calculation reveals the hybridization of Fe3$d$ states with those of Nb and O over the whole width of the valence band (see Fig.1). Moreover, several groups of localized impurity states are split off to form flat bands just above the Fermi level. Majority-spin $t_{2g}$ states are completely filled, whereas all other $d$-orbitals are roughly half-filled. Magnetic moment at Fe is 1.69 $\mu_B$ and exclusively related to the 3$d$ shell.

It may be noted that the $t_{2g}$ states remain relatively more localized than $e_g$, as should be expected already from fact that the spatial distribution of the former dominates along the line directed towards the interstitial between adjacent K atoms. On the contrary, $e_g$ states directly overlap with the $p$ shells of nearest oxygen atoms. This hybridization mediates the interaction between the $e_g$-impurity levels (for both spin directions) at adjacent Fe atoms which are situated only two lattice spacings apart. As a result, the $e_g$-related subbands are smeared so strongly that the band gap almost disappears. We assume that the 8×KNbO$_3$-supercell is too small for a realistic modeling of isolated Fe impurities.

The doubling of this supercell with the translation vectors (022), (202), (220) results in the $\sqrt{2}$ times increased distance between Fe atoms. The broadening of the $e_g$ states is then sufficiently decreased to form completely split-off discrete levels in the band gap. The system remains non-metallic, in contrast to the 40-atom supercell where a small DOS at
FIG. 1. Total and Fe3\textit{d}-partial DOS as calculated for 40-at. and 80-at. supercells of \textit{KNbO}_3 with single substitutional Fe impurity.
the Fermi level was present. Therefore, this larger 80-atom supercell seems already to be appropriate for the treatment of impurity problem. It should be noted however that the charge and magnetic moment at the Fe site are almost identical in the calculation with both supercells.

The number of electrons and magnetic moments within atomic spheres of Fe and its nearest neighbors of different types are shown in Table I for several numbers of extra electrons. With no extra electrons, the charge configuration of Fe is of course far from the nominal $3d^3$ as mentioned above in reference to a non-charge compensated case. The reason is, the electrons of the valence band which have been in perfect crystal localized at the Nb site, should be, roughly speaking, added to this number. Since KNbO$_3$ is not so strongly ionic, and because of our choice of atomic sphere radii, the electron numbers in Table I are close to those of neutral atoms. Magnetic moment, induced by that of the impurity, primarily resides on the first oxygen sphere.

III. LDA+$U$ TREATMENT

In a similar supercell calculation for Fe in MgO [13], it was found that the LDA calculation results in a physically wrong stable solution with zero magnetic moment, irrespectively of the supercell size. In the present system, Fe impurity has similar nearest neighborhood of oxygen octahedron, and the crystal field splits the $3d$-states into lower $t_{2g}$ and upper $e_g$ states in a similar way, but the solution is magnetic and stable. Apparently, the difference from the MgO:Fe case is in the missing nearest neighbors in the [110] direction in the perovskite lattice. In MgO, non-magnetic Mg atoms interact strongly with Fe $t_{2g}$ states and force the occupation numbers in both spin channels to become equal. This mechanism works in the LDA, because the potential acting on the $t_{2g}$ states is not dependent on their occupation, and dominates over the intraatomic exchange.

Although no obvious problem of such kind comes out for far Fe at the Nb site in KNbO$_3$, one should keep in mind that the treatment of localized $d$ states in the LDA may in principle be erroneous. A practically feasible way to deal with this problem is the LDA+$U$ approach, proposed by Anisimov et al. [14] and tested by now for many systems, including Fe oxides [15,16] and some perovskites [17]. The essence of the method is that for the states which are ad hoc declared as localized, the total-energy functional as provided by the LDA and casted in the form dependent on the total number of localized electrons is corrected depending on the actual occupation numbers of different localized orbitals. As a result, the potentials acting on localized states become occupation dependent, and the one-electron energies get accordingly corrected, thus lifting orbital degeneracies when physically motivated. Effective Coulomb interaction $U$ and effective intraatomic exchange $J$ enter as external parameters in a self-consistent cycle of LDA+$U$ calculation. These parameters can be determined from first principles (see, e.g., Ref. [18]), once the orbitals which should be treated as localized are selected. However, $U$ and $J$ are of essentially intraatomic character and may be largely transferred within many systems including the same chemical constituent with a priori localized states.

Solovyev et al. [20] thoroughly studied the applicability of LDA+$U$ in comparison with LDA to LaMO$_3$ ($M$=Ti–Cu) perovskite systems, where a similar problem of treating more
FIG. 2. Local 3d-DOS for charge configurations with 2 and 3 addition electrons per 80-at. supercell of KNbO$_3$:Fe, as calculated in the LDA and LDA+$U$. 

DOS (states/eV)

Energy (eV)

DOS (states/eV)

Energy (eV)
TABLE I. Charges $Q$ and magnetic moments $M$ within atomic spheres of Fe impurity and its several neighboring atoms as calculated for different number of added electrons

| extra $e$ | Fe $Q$ | Fe $M$ | O$_{xy}$ $Q$ | O$_{xy}$ $M$ | O$_{z}$ $Q$ | O$_{z}$ $M$ | Nb$_{xy}$ $Q$ | Nb$_{xy}$ $M$ | Nb$_{z}$ $Q$ | Nb$_{z}$ $M$ | K $Q$ | K $M$ |
|---------|--------|--------|--------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------|-------|
| 0       | 8.78   | 1.69   | 5.88         | 0.24        | 5.90        | 0.27        | 4.96        | 0.01        | 5.04        | −0.01      | 6.98  | 0.00 |
| 1       | 8.79   | 1.68   | 5.90         | 0.19        | 5.91        | 0.24        | 4.98        | 0.01        | 5.05        | 0.00        | 6.99  | 0.00 |
| 2       | 8.93   | 3.13   | 5.90         | 0.43        | 5.90        | 0.53        | 5.02        | 0.02        | 5.09        | 0.01        | 7.00  | 0.00 |
| 2 (+$U$)| 8.85   | 3.31   | 5.92         | 0.41        | 5.91        | 0.51        | 5.01        | 0.02        | 5.09        | 0.01        | 7.01  | 0.00 |
| 3       | 8.92   | 3.13   | 5.93         | 0.33        | 5.93        | 0.42        | 5.03        | 0.04        | 5.10        | 0.03        | 7.02  | 0.00 |
| 3 (+$U$)| 8.88   | 3.20   | 5.93         | 0.34        | 5.93        | 0.45        | 5.05        | 0.02        | 5.11        | 0.00        | 7.02  | 0.00 |

localized $t_{2g}$ and somehow less localized $e_g$ states of a 3$d$ constituent occurs. As apparently the most reasonable option (among others tested), the $t_{2g}$ states have been singled out as localized ones, to be treated according the prescription of the LDA+$U$ approach, while $e_g$ have been attributed to common band states well describable within the LDA. This segregation may prove useful for the Fe impurity as well. But as a first try, we treated all Fe3$d$ states as localized. Estimates of $U$ for Fe based on somehow different criteria vary from $\sim 9$ eV [20] to 5.1 eV [16]; we used in our calculation $U=6.8$ eV as estimated in Ref. [19], and $J=0.89$ eV. We did the LDA+$U$ calculations only for the systems with added 2 and 3 electrons, that correspond to experimentally expected (nominally) Fe$^{3+}$ and Fe$^{2+}$ configurations, correspondingly. The related lines of data in Table I are labeled (+$U$).

IV. OVERVIEW OF RESULTS

As is seen from Table I, the number of electrons on all constituents, at the exception of Fe, grows very smoothly with the extra background charge. As the first electron is added, nothing happens at the Fe site, and the extra electron goes completely into the valence band, resulting only in a slight shift of the Fermi energy but not visibly affecting the DOS. With the second extra electron, the Fermi level finally crosses the narrow majority-spin $e_g$ subband (Fig. 2). This increases the magnetic moment considerably (by less that $2\mu_B$, however, because the majority-spin $e_g$ states also contribute somehow to the already occupied valence band). The distribution of the impurity states in the minority-spin channel is affected only quantitatively. The third extra electron begins to populate the minority-spin $t_{2g}$ subband, but most part of it goes into the valence band, where the charge at all sites almost uniformly increases. It is noteworthy that the magnetic moment at O neighbors dramatically increases with the addition of the second electron, but comes back (and the charge increases, instead) with the addition of the third one. Since the states at the top of the valence band are of exclusively O2$p$ character (see, e.g., Ref. [24]), the drift of the $e_g$-subband below the Fermi level and into the valence band affects the majority-spin O2$p$ states most directly. The crossing of the Fermi level by minority-spin $t_{2g}$ subband contributes to the minority-spin O2$p$ subband and reduces the magnetic moment on oxygen atoms, increasing at the same time their occupation. At this point, the majority-spin $e_g$ subband enters the region of noticeable Nb contribution in the valence band and produces the peak of magnetic moment.

7
Comparing the results of LDA and LDA+\(U\) calculations (Fig. 2), one should keep in mind that the overall effect of the latter is the lowering the energies of occupied states and the upward shift of vacant ones. This is exactly what happens in the configuration with 2 extra electrons. Since essentially all majority-spin states are already occupied in this configuration and all minority-spin states empty, the inclusion of the \(U\)-correction has a negligible effect on all integral properties (both charges and moments). However, the exact position of the \(t_{2g}\)-impurity state is changed, that may give rise to the change in the optical absorption. The situation in the configuration with 3 extra electrons is completely different. Since here the minority-spin \(t_{2g}\) state is partly occupied in the LDA, in the LDA+\(U\) treatment the potentials acting on the \(xy\), \(xz\) and \(yz\) components of it become different, thus lifting the orbital degeneracy of these states and distorting the local DOS considerably.

Summarizing, our study of the electronic structure of Fe impurity in the Nb site of KNbO\(_3\) with the analysis of different charge compensation has shown, that only two considerably different configurations of impurity occur. The first one, with the magnetic moment \(~1.7\ \mu_B\), corresponds to the substitutional impurity without compensation – the situation that probably is not very common in reality. This configuration, however, survives under addition of one extra electron per impurity. Two extra electrons – or, equivalently, Fe impurity combined with a distant oxygen vacancy – induces a transition into the high-spin state with the magnetic moment \(~3.1\ \mu_B\), with the minority-spin \(t_{2g}\) level in the band gap. The charge and magnetic moment of this configuration remain intact with the addition of third extra electron, but the exact position of the level in the gap (probably, its splitting as well) may be affected. The last two configurations with 2 or 3 extra electrons correspond to the most practically relevant impurity configurations, referred to as Fe\(^{3+}\) and Fe\(^{2+}\). A more precise study of their energetics is possible with the use of a full-potential calculation scheme and simultaneous analysis of lattice relaxation around impurity and, optionally, oxygen vacancy.

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