LETTER TO THE EDITOR

Charge distribution and optical properties of F^+ and F centres in KNbO$_3$ crystals

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Abstract. Results of quantum chemical calculations for the F^+ and F centres in cubic and orthorhombic phases of a KNbO$_3$ perovskite ferroelectric are presented and analysed in the light of existing experimental literature. It is shown that one (two) electrons of the F^+ and F centres, respectively, are considerably delocalized, even in the ground state of defects, over the two Nb atoms nearest to the O vacancy, and other close atoms. They resemble more electron defects in partly covalent SiO$_2$ crystals (the so-called E$_1'$ centre) than F-type centres in ionic MgO crystals. We predict two or three absorption bands (depending on the crystalline phase) for each of the defects. The calculated absorption energies for the F^+ centre are by 0.3–0.4 eV lower than those for the F centre.

Perovskite-type KNbO$_3$ crystals have numerous electro-optic and non-linear optic applications [1]. As the temperature lowers, KNbO$_3$ undergoes a sequence of phase transitions, from paraelectric cubic phase to ferroelectric tetragonal (at 708 K), then to the orthorhombic (at 498 K), and lastly to the rhombohedral (at 263 K) phase. The atomic positions in all these phases have been determined experimentally in [2]. It is well understood now that its properties are considerably affected by defects and impurities. In particular, reduced KNbO$_3$ crystals (containing oxygen vacancies) reveal short-time photorefractive response to short-pulse excitation which could be used for developing fast optical correlators [3]. On the other hand, its use for light frequency doubling is seriously affected by the presence of unidentified defects responsible for induced IR absorption [4]. It is also well known that the photorefractive effect, particularly important for holographic storage, depends on the presence of impurities and defects [5].

The oxygen vacancy, V$_O$, is quite a common defect in many oxide crystals [6]. It could be formed under high-energy particle irradiation or during the reduction process. Normally, these defects effectively trap electrons and become either neutral or positively charged with respect to the lattice (the so called F centres or F^+ centres, respectively [7]). Only F^+ centres are paramagnetic, but optical absorption is expected from both centres. One should note that only in MgO do the F^+ and F absorption bands coincide in energy. There were a number of observations of F-type centres in oxides, including MgO, CaO, BaO, BeO, ZnO, ThO$_2$, Al$_2$O$_3$, Li$_2$O and GeO$_2$ [6–14]. The identification of the F and F^+ centres is usually based on analogy with MgO, CaO [8, 11] and Al$_2$O$_3$ [13]: usually, the F^+ absorption peak lies on the long-wavelength side of that for the F centre, its energy obeys the simple empirical (Mollwo-like) law discussed below, and the Stokes shift of the F^+ centre luminescence is smaller.

Recently, F-type centres were observed under electron irradiation in several perovskites: $LiNbO_3$ [15, 16], $BaTiO_3$ [17] and $KNbO_3$ [18]. The threshold energy values measured in these papers are consistent with the oxygen atom displacement. In $LiNbO_3$ F^+ and F absorption bands peak at 1.63 eV and 2.48 eV, respectively (see also [19]). The experimentally observed displacement energy implies a binding energy for oxygen of 64 eV for $KNbO_3$ and 57 eV for $LiNbO_3$, quite consistent with the value found for O displacement in other oxides, e.g., 60 eV for MgO [20] and 79 eV for Al_2O_3 [21].

To our knowledge, in niobate-type crystals so far there exisit only very simplified calculations of the F^+ centre absorption energy in $LiNbO_3$ and $LiTaO_3$ [22]. They are based on the point-ion or semi-continuum models, neglecting lattice relaxation around the defect and self-consistent treatment of the electronic density distribution. On the other hand, the qualitative theory for the F centres in perovskite ferroelectrics [23] predicts considerable delocalization of the electron density from V_O towards the two nearest Nb atoms.

To answer these questions, as well as to clarify an assignment of the 2.7 eV absorption band in $KNbO_3$ [18], in this letter we perform self-consistent calculations of the atomic and electronic structure for the F^+ and F centres in $KNbO_3$ crystals.

We use a simplified, quantum chemical version of the Hartree–Fock method known as the intermediate neglect of the differential overlap (INDO) [24, 25]. This approach has been applied very successfully to calculations for many pure and defective oxide crystals, including MgO [26], α-Al_2O_3 (corundum) [27], TiO_2 [28], etc. In the recent studies of the pure $KNbO_3$ and $KTaO_3$ crystals [29, 30] their electronic structure, the equilibrium ground state structure for several ferroelectric phases, as well as Γ-phonon frequences, were reproduced in surprisingly good agreement with both *ab initio* calculations and available experimental data.

The INDO calculation scheme and the relevant computer code CLUSTERD were discussed in detail in [24, 25, 29]. This code allows us to perform both the cluster and periodic system calculations containing tens and hundreds of atoms as well as to carry out automated geometry optimization which is especially important in defect calculations. To avoid a problem of the boundary conditions well known for a cluster model, we use here the supercell model which is $2 \times 2 \times 2$ extension of the primitive unit cell, i.e. containing 40 atoms. Detailed analysis of the $KNbO_3$ parameterization for the INDO method is presented in [29]. It should be remembered here that only in the latter paper was considerable covalency of the chemical bonding in pure $KNbO_3$ obtained: the effective atomic charges found using the Mulliken population analysis are (in units of $|e|$): +0.543 for K, +2.019 for Nb and −0.854 for O. (More about ionicity of solids and definition of effective atomic charges can be found in [31].) This is in agreement with the effective atomic charges found in the experimental study for $LiNbO_3$ [32]. A high degree of covalency of the Nb–O bond might be expected from the intuitive electronegativity considerations and the fact of a strong overlap between O 2p and Nb 4d orbitals and partial densities of states.

To simulate the F centre, we started with a 40-atom supercell from which we removed one of the O atoms. In the cubic phase all O atoms are equivalent and have the local symmetry C_{4v} whereas in the orthorhombic phase there are *two* kinds of non-equivalent O atom whose symmetry is lower, C_{2v} or C_s. After the O atom is removed, the atomic configuration of surrounding atoms is re-optimized via a search of the total energy minimum as a function of the atomic displacements from regular lattice sites. Calculation of the adiabatic energy curves for the ground and excited states permits us to find the optical absorption energy using the so-called ΔSCF procedure, according to which the E_{abs} sought for is the difference between the total energies for the ground and excited state with the defect geometry fixed as in the ground state (a vertical optical transition).

In the F^+ calculations, for the supercell neutrality one K atom distant from V_O was also removed. This results in a reduction of the defect symmetry and additional displacements of the two nearest Nb atoms along the (010) and (100) axes. To study this charge compensation effect, we performed two kinds of calculation for the F^+ centres: (i) allowing the two nearest neighbour Nb atoms (which remain equivalent) to displace along the (001) axis only (a *linear relaxation* valid in the limit of the large separation between the V_O and K vacancy), and (ii) allowing their non-linear displacements in an arbitrary direction.

To extend the basis set in the F-type centre calculation, additional 1s, 2p atomic orbitals were centred at the O vacancy. Their parameters were chosen close to those used by us in the F centre calculations in MgO [26]: the orbital exponents $\zeta(1s) = 0.65(au)^{-1}$, $\zeta(2p) = 0.50(au)^{-1}$, the relevant electronegativities are zero (1s) and -3 eV (2p), and the bonding parameters β are zero for both 1s and 2p orbitals, respectively. During the defect geometry optimization, we make no *a priori* assumptions on the electron density distrubution.

Let us discuss the results obtained for the two different $KNbO_3$ phases. The positions of 14 atoms surrounding the F and F^+ centre in a *cubic phase* after lattice relaxation to the miminum of the total energy are given in table 1. The conclusion could be drawn that the largest relaxation occurs for the two nearest Nb atoms which are strongly displaced outwards the O vacancy along the (001) axis. This is accompanied by much smaller, outward displacement of K atoms and by an inward displacement of O atoms. The two Nb atoms give the largest (80%) contribution to the lattice relaxation energy given in table 2 whereas the O atoms give most of the rest energy gain (1 eV). To check the effect of the supercell size, we made calculations for the $3 \times 3 \times 3$ extended unit cell. The results do not change noticeably.

In the F^+ centre the two nearest Nb atoms are relaxed by 35% less (mainly along the (001) axis) than in the F centre, with the total energy gain less by 0.94 eV. In the arbitrary relaxation case additional Nb displacements along the (010) and (100) axes are only 3% of that along the (001) axis which is accompanied by the additional energy gain of 0.01 eV. This clearly demonstrates that our model of charge compensation via the K vacancy works very well.

The analysis of the effective charges of atoms surrounding the F centre shows that of the two electrons associated with the removed O atom only $\approx -0.6|e|$ is localized inside the V_O and a similar amount of the electron density is localized by the two nearest Nb atoms.

For the F^+ centre these quantities are $-0.3|e|$ and $-0.3|e|$, respectively. Such a small portion of the electron density localized inside the O vacancy explains the large lattice deformation around the (formally neutral) F centre; the nearest cations are repelled from V_O which has a charge of $+1.4|e|$. This is in sharp contrast with our F centre calculations in MgO where both electrons are well localized and the lattice deformation is only 2% [26].

The F centre produces the local energy level, which lies approximately 0.6 eV above the top of the valence band. Its molecular orbital primarily contains contributions from the atomic orbitals of the same two nearest Nb atoms.

The *orthorhombic phase* of $KNbO_3$ is important since it is stable in a broad temperature range around room temperature and thus is subject to most studies and practical applications. The atomic positions for the *perfect* orthorhombic cell were calculated in the previous paper [29] and are reproduced at the top of table 3. The conclusion suggests that the agreement with the experimental data [2] is very good. The displacements of Nb atoms nearest to the V_O are plotted in table 3 for both kinds of F centre existing in this phase. In fact, their displacements are very similar in magnitude and also close to those found for the cubic phase. The relevant relaxation energies are slightly less than for the F centre in the cubic

Table 1. Coordinates of three kinds of 14 atoms surrounding F and F^+ centres placed at the coordinate origin in the cubic phase (in units of the lattice constant $a = 4.016$ Å).

F centre without additional AO						
Nb	0.00000	0.00000	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.00000$	$\Delta_z = 0.08319$
K	$\pm(\frac{1}{2} + \Delta_x)$	$\pm(\frac{1}{2} + \Delta_y)$	0.00000	$\Delta_x = 0.01324$	$\Delta_y = 0.01324$	$\Delta_z = 0.00000$
O	$\pm(\frac{1}{2} - \Delta_x)$	0.00000	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.02372$	$\Delta_y = 0.00000$	$\Delta_z = 0.00447$
O	0	$\pm(\frac{1}{2} - \Delta_y)$	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.02372$	$\Delta_z = 0.00447$
F centre with additional AO						
Nb	0.00000	0.00000	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.00000$	$\Delta_z = 0.06550$
K	$\pm(\frac{1}{2} + \Delta_x)$	$\pm(\frac{1}{2} + \Delta_y)$	0.00000	$\Delta_x = 0.00920$	$\Delta_y = 0.00920$	$\Delta_z = 0.00000$
O	$\pm(\frac{1}{2} - \Delta_x)$	0.00000	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.01920$	$\Delta_y = 0.00000$	$\Delta_z = 0.00334$
O	0	$\pm(\frac{1}{2} - \Delta_y)$	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.01920$	$\Delta_z = 0.00334$
F^+ centre without additional AO (non-linear Nb relaxation)						
Nb	Δ_x	Δ_y	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00150$	$\Delta_y = 0.00150$	$\Delta_z = 0.05231$
F^+ centre without additional AO (linear Nb relaxation)						
Nb	0.00000	0.00000	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.00000$	$\Delta_z = 0.05231$
K	$\pm(\frac{1}{2} + \Delta_x)$	$\pm(\frac{1}{2} + \Delta_y)$	0.00000	$\Delta_x = 0.00894$	$\Delta_y = 0.00894$	$\Delta_z = 0.00000$
O	$\pm(\frac{1}{2} - \Delta_x)$	0.0000	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.01742$	$\Delta_y = 0.00000$	$\Delta_z = 0.00286$
O	0	$\pm(\frac{1}{2} - \Delta_y)$	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.01742$	$\Delta_z = 0.00286$
F^+ centre with additional AO (non-linear Nb relaxation)						
Nb	Δ_x	Δ_y	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00120$	$\Delta_y = 0.00120$	$\Delta_z = 0.04180$
F^+ centre with additional AO (linear Nb relaxation)						
Nb	0.00000	0.00000	$\pm(\frac{1}{2} + \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.00000$	$\Delta_z = 0.04180$
K	$\pm(\frac{1}{2} + \Delta_x)$	$\pm(\frac{1}{2} + \Delta_y)$	0.00000	$\Delta_x = 0.00715$	$\Delta_y = 0.00715$	$\Delta_z = 0.00000$
O	$\pm(\frac{1}{2} - \Delta_x)$	0.0000	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.01361$	$\Delta_y = 0.00000$	$\Delta_z = 0.00227$
O	0	$\pm(\frac{1}{2} - \Delta_y)$	$\pm(\frac{1}{2} - \Delta_z)$	$\Delta_x = 0.00000$	$\Delta_y = 0.01361$	$\Delta_z = 0.00227$

Table 2. Calculated absorption (E_{abs}, eV) and Nb relaxation (E_{rel}, eV) energies for the F^+ and F centres for the cubic and the orthorhombic phases.

Symmetry, phase	E_{abs}		E_{rel}	
F centre				
C_{4v}, cubic	2.73	2.97	—	3.70
C_s, orthorhombic	2.56	3.03	3.10	3.60
C_{2v}, orthorhombic	2.72	3.04	3.11	3.60
F^+ centre (non-linear Nb relaxation)	2.34	2.66	2.67	2.76
F^+ centre (linear Nb relaxation)	2.34	2.66	—	2.75

phase. Since the effect of phase transition on the local lattice deformation is small, we studied its consequences only for the F centre.

Let us analyse the *optical properties* of the defects under study. Because of the C_{4v} local symmetry of the F-type centres in the $KNbO_3$ cubic phase, its excited 2p-type state splits into two levels, one of which remains twofold degenerate. Our ΔSCF calculations predict the two pairs of the absorption bands given in table 2. When the nearest Nb atoms in the F^+ centre are allowed to displace non-linearly due to the presence of charge compensating

K vacancy, the degenerate highest excited state splits off into the two very close levels (separated by only 0.01 eV).

Around room temperature, in the orthorhombic phase, there exist two kinds of F-type centre associated with two non-equivalent O atoms shown in table 3 and revealing the C_{2v} and C_s symmetry. The corresponding three absorption bands for F centres are plotted in table 2. Their difference is the largest for the lowest in energy bands (0.16 eV) and negligible for the other two bands.

Table 3. Atomic coordinates for a perfect orthorhombic phase of KNbO$_3$ (in terms of lattice parameters $a = 3.973$ Å, $b = 5.695$ Å, $c = 5.721$ Å INDO calculated in [29], as well as the positions of the two Nb atoms nearest to the F centre related to a O(I) vacancy (point symmetry C_{2v}) and O(II) vacancy (symmetry C_s, respectively).

Atom	a	b	c	Δ	
Perfect crystal					
K	0	0	Δ_z	$\Delta_z = 0.0209$	
Nb	$\frac{1}{2}$	0	$\frac{1}{2}$		
O$_I$	0	0	$\frac{1}{2} + \Delta_z$	$\Delta_z = 0.0347$	
O$_{II}$	$\frac{1}{2}$	$\frac{1}{4} + \Delta_y$	$\frac{1}{4} + \Delta_z$	$\Delta_y = -0.0028$	$\Delta_z = 0.0347$
O$_{II}$	$\frac{1}{2}$	$\frac{3}{4} - \Delta_y$	$\frac{1}{4} + \Delta_z$	$\Delta_y = -0.0028$	$\Delta_z = 0.0347$
F centres of C_{2v} symmetry: no additional AO					
Nb(I)	$\frac{1}{2} + \Delta_x$	0	$\frac{1}{2} + \Delta_z$	$\Delta_x = 0.08333$	$\Delta_z = 0.0132$
Nb(II)	$-\frac{1}{2} + \Delta_x$	0	$\frac{1}{2} + \Delta_z$	$\Delta_x = -0.08333$	$\Delta_z = 0.0132$
F centres of C_{2v} symmetry with additional AO					
Nb(I)	$\frac{1}{2} + \Delta_x$	0	$\frac{1}{2} + \Delta_z$	$\Delta_x = 0.0656$	$\Delta_z = 0.0106$
Nb(II)	$-\frac{1}{2} + \Delta_x$	0	$\frac{1}{2} + \Delta_z$	$\Delta_x = -0.0656$	$\Delta_z = 0.0106$
F centres of C_s symmetry: no additional AO					
Nb(I)	$\frac{1}{2}$	Δ_y	$\frac{1}{2} + \Delta_z$	$\Delta_y = -0.0468$	$\Delta_z = 0.02502$
Nb(II)	$-\frac{1}{2}$	$\frac{1}{2} + \Delta_y$	Δ_z	$\Delta_y = 0.0244$	$\Delta_z = -0.03735$
F centres of C_s symmetry with additional AO					
Nb(I)	$\frac{1}{2}$	Δ_y	$\frac{1}{2} + \Delta_z$	$\Delta_y = -0.0361$	$\Delta_z = 0.0192$
Nb(II)	$-\frac{1}{2}$	$\frac{1}{2} + \Delta_y$	Δ_z	$\Delta_y = 0.0187$	$\Delta_z = -0.0286$

In a number of crystalline oxides (MgO, CaO, SrO, BeO, Al$_2$O$_3$, MgAl$_2$O$_4$, Y$_3$Al$_5$O$_{15}$ [33] as well as in LaMgAl$_{11}$O$_{19}$ [34]) the F$^+$ absorption energy obeys a simple law:

$$E_{abs}(\text{eV}) = 44.4a^{-2} - 3.5a^{-1}$$

where $a = n^{-1/3}$ is a mean distance between two O atoms and n their concentration in the lattice.

Application of this relation to KNbO$_3$ gives, however, an absorption energy greatly exceeding the optical gap (3.8 eV). In our opinion, this demonstrates that niobates are a special case. Indeed, our results for the electronic density distribution are in a sharp contrast with what is known for the F centres in ionic oxides (in particular, in MgO [6, 7, 26]) where the two electrons are well localized by the V$_O$ in its ground state. Evidently, this discrepancy arises from a considerable degree of covalency of the chemical bonding of KNbO$_3$ which is neglected in most models of defects in this material (as well as in similar ABO$_3$ perovskites, e.g. [19]); the only exception we know is the X$_\alpha$ cluster calculation of the F centre in LiNbO$_3$ [35]. Electron defects similar to what we have observed are known,

in particular, in partly covalent SiO_2 crystals (e.g., in the so-called E'_1 centre an electron is also not localized inside V_O but sits on the sp^3 orbital of a neighbouring Si atom [36]).

In summary, we found that the ground state of the F centre is associated with a strong *symmetrical* relaxation of the two nearest Nb atoms outwards the O vacancy. These Nb atoms remain identical, i.e. we did not see formation of dipole moments of the Nb_1–V_O–Nb_2 type, as suggested in [23].

The relevant lattice relaxation energy of 3–4 eV (table 2) is typical for point defects in ionic and partly-ionic solids and by several orders of magnitude larger than the tiny energy gain due to phase transitions (meV per cell).

We assume that the 2.7 eV absorption band observed in electron irradiated crystals [18] is due to the F-type centres, and predict existance of two more absorption bands for both F and F^+ centres at room temperature.

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