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## Semi-empirical calculations of the Nb-ion positions in doped $\text{KTaO}_3$ crystals

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**Abstract.** The atomic and electronic structures of Nb impurities in doped perovskite  $\text{KTaO}_3$  crystals are calculated using the semi-empirical quantum chemical method of the intermediate neglect of the differential overlap (INDO) and a supercell model. When seven Ta ions are replaced by seven Nb ions, the latter clearly demonstrate self-ordering effects which are related to the experimentally observed impurity-induced phase transition.

A single Nb impurity reveals an off-centre displacement which is very close to that found in XAFS experiments. The relevant energy gain is very small, approximately 0.0375 eV, which is much smaller than the Nb-clustering energy gain (0.12 eV). These results led us to the conclusion that such self-ordered high-symmetry seven-ion clusters are stable in a  $\text{KTaO}_3$  matrix.

### 1. Introduction

Mixed potassium tantalate–niobate crystals ( $\text{KTN}$ ,  $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ ) are of great interest for many electro-optical and holographic applications [1]. Pure  $\text{KTaO}_3$  is an incipient ferroelectric which becomes ferroelectric even for very low Nb doping,  $x = 0.01$ . This gave rise to discussion about the nature of the phase transition in  $\text{KTN}$  [2]. By means of x-ray photoelectron spectroscopy (XPS) it was shown [3] that Ta ions are replaced by Nb ions. On the other hand, XAFS measurements [2] demonstrated that the Nb is at off-centre positions. Its [111] displacement is 0.145 Å at 70 K, and changes by less than 20 per cent as the temperature increases to the room temperature. The purpose of this paper is the calculation of the Nb-impurity positions in  $\text{KTaO}_3$  for an isolated Nb impurity and for clustered Nb impurities. For this purpose, the semi-empirical, quantum chemical method of the intermediate neglect of the differential overlap (INDO) [4] has been used in our study. The modification of the INDO method for ionic solids is described in detail in references [5–7]. This method has been demonstrated to give very good results in previous calculations for defects, both in the bulk and on the surface, for many oxide materials [5–11], including pure  $\text{KNbO}_3$  and  $\text{KTaO}_3$  perovskites [12, 13] and defects—F centres and hole polarons in  $\text{KNbO}_3$ , as well as Li impurities in  $\text{KTaO}_3$  [13–15]. Furthermore, it provides the basis for easy calculations for a cluster embedded in the electrostatic field of the rest of the crystal and for periodic systems, using the large-unit-cell (LUC) model. The INDO method is based on the Hartree–Fock formalism, and allows self-consistent calculations of the atomic and electronic structure of pure and defect-containing crystals to be carried out.

## 2. Method

The Fock matrix elements in the modified INDO approximation [5–7] contain a number of semi-empirical parameters. The orbital exponent  $\zeta$  enters the radial part of the Slater-type atomic orbitals:

$$R_{nl}(r) = (2\zeta)^{n+1/2} [(2n)!]^{-1/2} r^{n-1} \exp(-\zeta r) \quad (1)$$

where  $n$  is the main quantum number of the valence shell. The diagonal matrix elements of the interaction of an electron occupying the  $\mu$ th valence atomic orbital on atom A with its own core are taken as

$$U_{\mu\mu}^A = -E_{\text{neg}}^A(\mu) - \sum_{v \in A} \left( P_{vv}^{(0)A} \gamma_{\mu v} - \frac{1}{2} P_{vv}^{(0)A} K_{\mu v} \right) \quad (2)$$

where  $P_{\mu\mu}^{(0)A}$  are the (initial guesses for the) diagonal elements of the density matrix, and  $\gamma_{\mu v}$  and  $K_{\mu v}$  are one-centre Coulomb and exchange integrals, respectively.  $E_{\text{neg}}^A(\mu)$  is the initial guess for the  $\mu$ th atomic orbital energy. The interaction of an electron on the  $\mu$ th atomic orbital belonging to the atom A with the core of another atom B reads

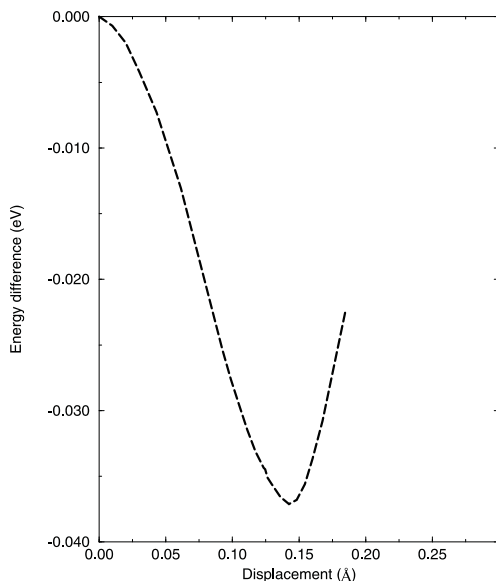
$$V_{\mu}^B = Z_B \left\{ 1/R_{AB} + [\langle \mu\mu | \nu\nu \rangle - 1/R_{AB}] \exp(-\alpha_{AB} R_{AB}) \right\} \quad (3)$$

where  $R_{AB}$  is the distance between atoms A and B,  $Z_B$  is the core charge of atom B, and parameter  $\alpha_{AB}$  describes the non-point character of this interaction. The resonance-integral parameter  $\beta_{\mu\nu}$  enters the off-diagonal Fock matrix elements for the spin component  $u$ :

$$F_{\mu\nu}^u = \beta_{\mu\nu} S_{\mu\nu} - P_{\mu\nu}^u \langle \mu\mu | \nu\nu \rangle \quad (4)$$

where the  $\mu$ th and  $\nu$ th atomic orbitals are centred at different atoms,  $S_{\mu\nu}$  is the matrix describing the overlap between them, and the  $\langle \quad | \quad \rangle$  are two-electron integrals. Thus the INDO parametrization scheme contains the following set of parameters per atom:  $\zeta$ ,  $E_{\text{neg}}$ ,  $P^{(0)}$ ,  $\alpha$ ,  $\beta$ . In this study, to avoid a boundary condition problem for a cluster in partly covalent KNbO<sub>3</sub>, a 135-atom LUC was used for an isolated Nb impurity (which is the  $3 \times 3 \times 3$  extension of the primitive unit cell of five atoms). This means that Nb impurities are distributed periodically, with a distance between the two nearest Nb ions of  $3a_0$ . We performed our INDO calculations using the experimental KTaO<sub>3</sub> lattice constant (extrapolated to zero temperature) of 3.983 Å. We used an even larger, 320-atom LUC (extended by  $4 \times 4 \times 4$ ) for Nb clusters. It is clear that no *ab initio* methods could be used at present for such large-scale computer simulations with defect geometry optimization. The valence basis set included 4s, 4p atomic orbitals for K, 2s, 2p orbitals for O, 5s, 5p, 4d atomic orbitals for Nb, and 6s, 6p, 5d atomic orbitals for the Ta atom. The relevant detailed analysis of the INDO parametrization for KNbO<sub>3</sub> and KTaO<sub>3</sub> is given in references [12, 13]. We merely note here that the INDO parametrization reproduces surprisingly well the results of an *ab initio* LDA study of the electronic structure, including the equilibrium ground state for several ferroelectric phases, as well as  $\Gamma$  phonon frequencies. Covalency effects could be seen from the static effective charges on the atoms: 0.62  $e$  for K, 2.23  $e$  for Ta, and  $-0.95 e$  for O, which are far from the values expected from the ionic model ( $+1 e$ ,  $+5 e$ , and  $-2 e$ , respectively). These charges show slightly higher ionicity in KTaO<sub>3</sub> as compared with the effective charges 0.54  $e$  for K, 2.02  $e$  for Nb, and  $-0.85 e$  for O in KNbO<sub>3</sub> [12]. (More about the ionicity of solids and the definition of effective atomic charges can be found in reference [16].) The band gap in KTaO<sub>3</sub> as obtained by the INDO method has the value 6.7 eV [13], which is close to, but larger than, the value of 6.1 eV calculated by the INDO method for KNbO<sub>3</sub> [12]. The absolute value of the gap in the one-electron energy spectrum is known to come out as systematically larger in the Hartree–Fock formalism as

compared with spectroscopic data, because the unscreened Coulomb interaction shifts the unoccupied states too high in energy.



**Figure 1.** The total energy versus the [111] off-centre displacement of a Nb impurity in  $\text{KTaO}_3$  crystals.

### 3. Results

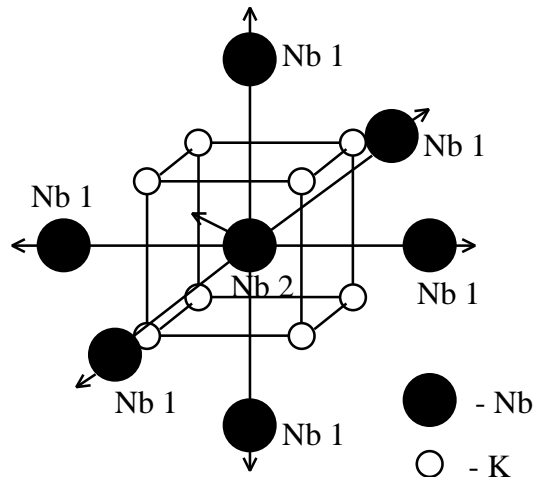
#### 3.1. The single Nb ion

Figure 1 shows the total energy for a 135-atom cluster modelling an *isolated* Nb impurity as a function of its [111] off-centre displacement. The conclusion can be drawn that the calculated displacement of 0.146 Å is very close to the experimental XAFS finding at 70 K [2]. The relevant energy gain is very small, approximately 0.0375 eV, which is typical for the Nb displacements calculated earlier for different ferroelectric phases of  $\text{KNbO}_3$  [12].

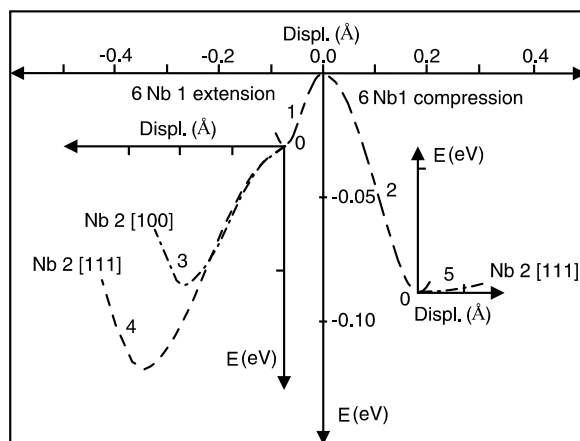
#### 3.2. Nb clusters

In the next step, in the *Nb-cluster* calculations we have extended the primitive  $\text{KTaO}_3$  unit cell by  $4 \times 4 \times 4$ , i.e. to 64 times its size, which is equivalent to carrying out the band-structure calculations at 64  $k$ -points in the Brillouin zone. In order to study cooperative displacements (self-ordering) of Nb impurities in  $\text{KTaO}_3$ , we replaced, in our extended unit cell containing 320 atoms, seven Ta atoms by seven Nb atoms, as is shown schematically in figure 2.

After doing this, in order to find the energy minima of the Nb clusters in  $\text{KTaO}_3$ , we allowed six Nb atoms to relax symmetrically towards the central Nb atom. The positions of the K, Ta, and O atoms were kept fixed. The results of our calculations show that six Nb atoms are shifted inwards towards the central Nb atom by 0.187 Å, lowering the total energy of the system by 0.088 eV. However, we discovered that symmetric displacements of six



**Figure 2.** Asymmetric relaxation in a Nb cluster containing seven Nb atoms inside  $\text{KTaO}_3$ , calculated using a  $4 \times 4 \times 4$ -extended unit cell, containing 320 atoms; six atoms relax outwards from the central Nb atom, which is displaced away from the centre along the [100] or [111] direction.



**Figure 3.** Displacement energies of six Nb atoms relaxed outwards (curve 1) and inwards (curve 2) with respect to the centre of the seven-Nb-atom cluster. The central Nb atom is displaced away from the centre in the [100] and [111] directions (curves 3 and 4, respectively) in the case of symmetric extension of the cluster, but it remains at the centre (curve 5) in the case of inward cluster relaxation.

Nb atoms outwards by  $0.073 \text{ \AA}$  from the central Nb atom (see figure 2), thus lowering the total energy of the system by  $0.03 \text{ eV}$  (see figure 3), are also energetically favourable. In this case, when six Nb atoms are shifted outwards from the central Nb atom, the central Nb atom undergoes an off-centre displacement from the on-site position in the [111] direction by  $0.27 \text{ \AA}$ , and this is accompanied with an additional total energy gain of  $0.09 \text{ eV}$ —to give a total energy reduction of  $0.12 \text{ eV}$ . This configuration corresponds to the ground-state multiplet.

The central Nb atom also reveals instability in the [100] direction. The shift of the

central Nb ion in the [100] direction by  $0.192 \text{ \AA}$  lowers the cluster energy additionally by  $0.056 \text{ eV}$ , in the case in which six Nb atoms are shifted outwards the central Nb atom—to give a total energy reduction of  $0.086 \text{ eV}$ . Nevertheless the total cluster-structure-induced energy lowering in the ground state, which corresponds to the situation in which six Nb atoms are symmetrically relaxed outwards from the centre of Nb cluster, and the central Nb atom is displaced away from the centre in the [111] direction ( $0.12 \text{ eV}$ ), turns out to be energetically more favourable (see figure 3).

According to our calculations, in the case in which six Nb atoms are in the energy-minimum state arising from a symmetric displacement of six Nb atoms towards the central Nb atom (which could be treated as an excited state of the Nb cluster), the central Nb atom exhibits on-site properties (see figure 3).

#### 4. Discussion

The interpretation of impurity-induced ferroelectric phase transitions in terms of on-site impurities (like  $\text{Ba}^{2+}$  impurities in the incipient ferroelectric  $\text{SrTiO}_3$ ) or weak off-centre impurities (like  $\text{Nb}^{5+}$  impurities in incipient ferroelectric  $\text{KTaO}_3$ , and  $\text{Ca}^{2+}$  impurities in  $\text{SrTiO}_3$ ) had been suggested recently on the basis of the so-called *self-ordered cluster model* [17], extended and applied to Ta clusters in  $\text{KNbO}_3$  in reference [18]. The main prediction of this model is that self-ordered clusters of the second component (Nb in  $\text{KTaO}_3$ ) will form, which we have indeed observed in our calculations. Such self-ordered clusters of the second component in solid solutions based on ferroelectric perovskites have their own degrees of freedom (of order–disorder as well as displacive types). The percolation of the corresponding local order parameters as well as dynamical percolation of the soft, low-frequency local vibrations can lead to a *cooperative behaviour* which finally (at a definite concentration of the second component) induces a ferroelectric phase transition.

Our numerical INDO calculations have demonstrated that a single Nb impurity undergoes an off-centre displacement which is very close to that found in XAFS experiments [2]. The relevant energy gain is very small, approximately  $0.0375 \text{ eV}$ , which is much smaller than the Nb-clustering energy gain ( $0.12 \text{ eV}$ ). These results led us to the conclusion that such self-ordered high-symmetry seven-ion clusters are stable in a  $\text{KTaO}_3$  matrix.

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