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QUANTUM CHEMICAL CALCULATIONS OF KTN SOLID SOLUTIONS

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The results of semi-empirical calculations for perovskite $\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$ (KTN) solid solutions are presented for $x = 0.04, 0.11, 0.89,$ and 0.96 . Quantum chemical method of the Intermediate Neglect of the Differential Overlap (INDO) was combined with 135- and 320-atom supercells. Analysis of the optimised atomic and electronic structure has clearly demonstrated that several nearest Nb atoms substituting for Ta in KTaO_3 — unlike Ta impurities in KNbO_3 — reveal the self-ordering effect, which probably triggers the ferroelectricity observed in KTN.

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1. INTRODUCTION

PEROVSKITE-TYPE oxides like KNbO_3 , KTaO_3 and their solid solutions $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (KTN) are important for many applications including electro-optics, holography, and second-harmonic generation [1]. As the temperature decreases, KNbO_3 goes through three ferroelectric phase transitions, whereas KTaO_3 is only an “incipient” ferroelectric which becomes ferroelectric already at very low Nb impurity concentrations, $x \geq 0.01$. This raises a question about the nature of the phase transition in KTN [2]. X-ray photoelectron spectroscopy (XPS) has shown [3] that Ta ions are replaced by the Nb ions. Additionally XAFS measurements [2] have demonstrated that the Nb sits in off-center position. Its [111] displacement is 0.145 \AA at 70 K, and changes by less than 20 percent as the temperature increases to the room temperature.

The purpose of this Communication is comparative calculations of the Nb impurities in KTaO_3 and vice versa, Ta in KNbO_3 , both for an isolated impurity and for clustered impurities in a cubic, paraelectric phase of these crystals. For this purpose, the semi-empirical, quantum chemical method of the Intermediate Neglect of the Differential Overlap (INDO) [4] has been used. The method is based on the Hartree-Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defec-

tive crystals. The modification of the standard INDO method for ionic solids is described in detail in Ref. [5–7]. This method has demonstrated very good results in previous calculations of defects, both in the bulk and on the surface, in many oxide materials [5–11], including pure KNbO_3 and KTaO_3 perovskites [12, 13] and defects — F centers and hole polarons — in KNbO_3 , as well as Li impurities in KTaO_3 [13–15]. The more so, it permits easy calculations for both a cluster embedded into the electrostatic field of the rest of the crystal and for periodic systems, using the supercell model.

To avoid a boundary condition problem for a cluster in partly covalent perovskites, a 135-atom supercell was used for modeling an *isolated* Nb or Ta impurity (which is the $3 \times 3 \times 3$ extension of the primitive unit cell of five atoms). This means that impurities are distributed periodically, with the distance between the two nearest impurity ions of $3a_0$. We performed our INDO calculations at the experimental KTaO_3 and KNbO_3 lattice constants (extrapolated to zero temperature) of $a_0 = 3.983 \text{ \AA}$ and 4.016 \AA , respectively. We used much larger, 320-atom ($4 \times 4 \times 4$) supercells for seven-atom Nb (Ta) *clusters*. The relevant isolated and clustered impurity concentrations are 4 % and 11 %, respectively. 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 (AO)

for K, $2s$, $2p$ for O, $5s$, $5p$, $4d$ for Nb and $6s$, $6p$, $5d$ for the Ta atom.

A key factor for success of any semi-empirical method is a proper parameterization which should be done for every new class of materials. The relevant detailed analysis of the development of the INDO parameterization for pure KNbO_3 and KTaO_3 is given in Refs. [12, 13]. Note here only that the INDO method reproduced surprisingly well both available experimental data and results of *ab initio* LDA calculations, the INDO results are also relatively stable against some variation of parameters. Not only the very effect of a ferroelectric instability of KNbO_3 due to off-center displacement of Nb atoms from the lattice sites but also the relative magnitudes of the relevant energy gains for the [100], [110], and [111] Nb displacements are consistent with the order of the stability of the tetragonal, orthorhombic and rhombohedral ferroelectric phases, respectively as the temperature lowers. This is a very non-trivial achievement since the typical energy gain due to the Nb off-center displacement is as small as several mRy per unit cell. The calculated frequencies of the transverse-optic (TO) phonons at the Γ point in the BZ of cubic and rhombohedral KNbO_3 and the atomic coordinates in the minimum energy configuration for the orthorhombic and rhombohedral phases of KNbO_3 are also in good agreement with experiment thus indicating that a very successful INDO parameterization has been achieved. Frozen-phonon calculation for T_{1u} and T_{2u} modes of cubic KTaO_3 are also in good agreement with experiment.

Covalency effects in the chemical bonding could be seen from the calculated (static) effective charges on atoms: $0.62 e$ for K, $2.23 e$ for Ta and $-0.95 e$ for O in KTaO_3 , which are far from expected in the purely ionic model ($+1 e$, $+5 e$ and $-2 e$, respectively) often used. These charges show slightly higher ionicity in KTaO_3 as compared with the relevant effective charges in KNbO_3 : $0.54 e$ for K, $2.02 e$ for Nb and $-0.85 e$ for O [12]. (More about ionicity of solids and definition of effective atomic charges see in Ref. [16]).

2. RESULTS

2.1. Single Nb ion

Let us start discussion of results with KTaO_3 doped with Nb. Curve 1 in Fig. 1 shows the total energy for a 135-atom cluster modelling an *isolated* Nb impurity as a function of its [111] off-center displacement. The immediate conclusion can be drawn that the calculated displacement of 0.146 \AA is very close to the experimental XAFS finding at 70 K [2]. The relevant energy

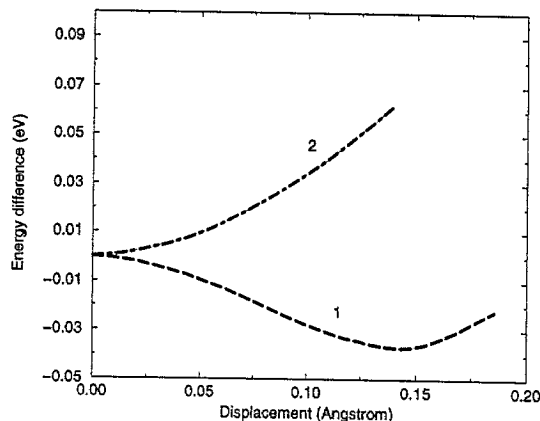


Fig. 1. Total energy vs the [111] off-center displacement of an isolated Nb impurity in KTaO_3 crystals (curve 1) and Ta in KNbO_3 (curve 2).

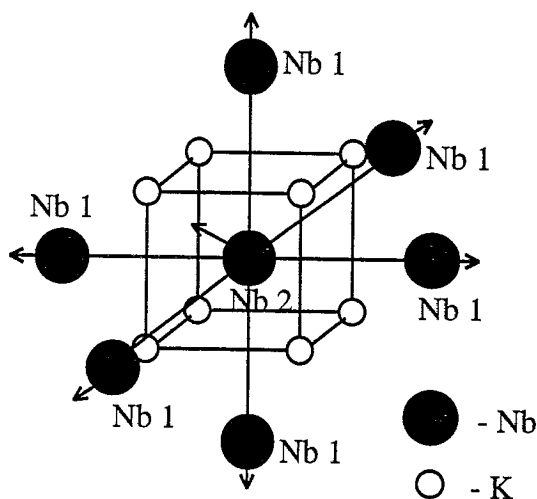


Fig. 2. Sketch of an asymmetric relaxation in a Nb cluster containing seven nearest-neighbour Nb atoms in KTaO_3 , calculated using a $4 \times 4 \times 4$ extended unit cell, containing 320 atoms; six Nb 1 atoms relax outwards the central Nb 2 atom which is off-center displaced along the [100] or [111] direction.

gain is very small, approximately 0.0375 eV , which is typical for the Nb displacement calculated earlier for different ferroelectric phases of KNbO_3 [12].

2.2. Nb clusters

Next, in the *Nb cluster* calculations we have extended the primitive KTaO_3 unit cell, by $4 \times 4 \times 4$ i.e. 64 times. In order to study possible *cooperative* displacements (self-ordering) of Nb impurities in KTaO_3 , we replaced in our extended unit cell (containing 320 atoms) seven Ta atoms by seven Nb atoms, as it is shown schematically in Fig. 2.

After doing so, in order to find energy minima of Nb-clusters in KTaO_3 we allowed six Nb 1 atoms to

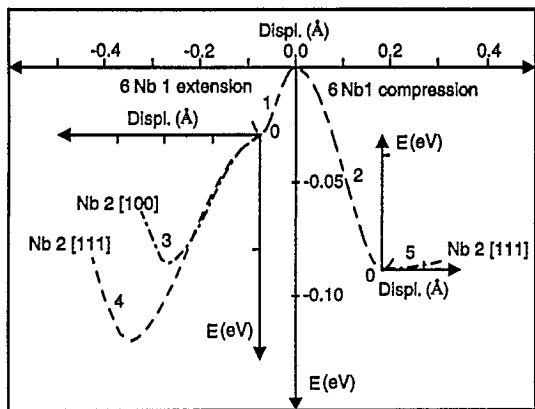


Fig. 3. Total energy vs displacement of six Nb atoms in KTaO_3 which are relaxed outwards (curve 1) and inwards (curve 2) with respect to the centre of the seven-Nb atom cluster. The central Nb atom prefers an off-center position in the [100] and [111] directions, (curves 3 and 4, respectively). In the case of symmetrical inward compression of impurity cluster it remains on-center (curve 5).

relax symmetrically towards the central Nb 2 atom. The positions of K, Ta and O atoms were kept fixed. Results of our calculations show that six Nb atoms are shifted inwards the central Nb atom by 0.187 \AA , lowering the total energy of a system by 0.088 eV (curve 2 in Fig. 3). However, we discovered another energetically favourable symmetric displacements of six Nb atoms outwards by 0.073 \AA from the central Nb atom (curve 1 in Fig. 3) lowering the total energy of a system by 0.03 eV . In the case when six Nb atoms are shifted outwards from the central Nb atom, the central Nb 2-atom reveals the off-center displacement from the on-site position in the [111] direction by 0.27 \AA , accompanied with the additional total energy gain of 0.09 eV - to give a total energy reduction of 0.12 eV (curve 4).

The central Nb 2 atom reveals another instability in the [100] direction; its shift in this direction by 0.192 \AA lowers the total energy additionally by 0.056 eV (provided, six Nb 1 atoms are relaxed outwards) thus giving a total energy reduction of 0.086 eV (curve 3). That is, the atomic configuration of impurities, when six Nb 1 atoms are symmetrically relaxed outwards the centre of Nb-cluster, and the central Nb 2 atom simultaneously becomes off-center in the [111] direction, turns out to be the energetically most favourable (energy gain is 0.12 eV). In contrast, in the configuration where six Nb 1 atoms are in the energy minimum at a symmetric inward displacement, the central Nb 2 atom remains on-center (curve 5 in Fig. 3).

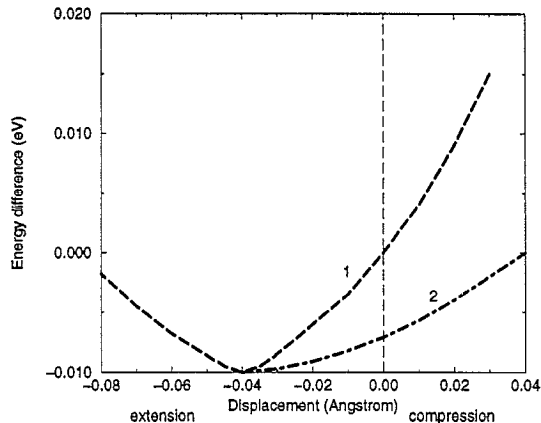


Fig. 4. Total energy vs displacement of six nearest-neighbour Ta atoms in KNbO_3 (see Fig. 2) which are relaxed outwards and inwards with respect to the Ta atom in the coordinate origin (curve 1). Curve 2 shows the additional effect of the central Ta atom displacement along the (111) axis when six Ta atoms are fixed at the optimised configuration corresponding to the minimum in curve 1.

3. DISCUSSION

Calculations for Ta impurities in KNbO_3 demonstrate their qualitatively different behaviour. First of all, an isolated Ta impurity retains its on-site position (curve 2 in Fig. 1) — unlike Nb atom in KTaO_3 (curve 1), or Nb atoms in pure KNbO_3 at low temperatures [12]. Secondly, our modeling of an impurity cluster containing seven Ta atoms — similar to Nb clusters in KTaO_3 — shows clearly that the total energy minimum corresponds to the symmetrically (0.04 \AA) extended configuration of 6 Ta atoms with the seventh Ta in the coordinate origin (curve 1 in Fig. 4). If the central Ta atom is additionally displaced along the (111) axis, the system's energy monotonously increases (curve 2) — unlike the case of Nb in KTaO_3 when displacement of central atom results in an additional energy gain (curve 4 in Fig. 3).

In conclusion, we would like to stress that our numerical INDO calculations have demonstrated that a single Nb impurity in KTaO_3 reveals an off-center displacement which is very close to that found in XAFS experiments [2]. The relevant energy gain is very small, approximately 0.0375 eV which is much smaller than the Nb-clustering energy gain (0.12 eV). Close Nb impurities are self-ordered and reveal a cooperative behaviour. This probably triggers the KTN ferroelectric phase transition. In contrast, Ta impurities in KNbO_3 reveal no self-ordering. Qualitatively different behaviour of Nb and Ta atoms could be caused by a tiny difference in their chemical bonding with other atoms, first of all oxygens. A comparative

analysis of the effective charges show that the charge for a single Ta impurity in KNbO_3 is $2.15 e$ whereas that of a host Nb atom is $2.02 e$. This confirms conclusion [13] about higher ionicity of Ta in a comparison with Nb atoms in pure crystals. In its turn, the effective charge of a single Nb impurity in KTaO_3 is $2.08 e$ (whereas for a host Ta atoms the charge is $2.23 e$). The effective charge of Ta ions in seven-ion cluster in KNbO_3 is $2.18 e$, and that of Nb ion in seven-ion cluster in KTaO_3 is $2.06 e$, again smaller.

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