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LETTER TO THE EDITOR

Quantum chemical modelling of perovskite solid solutions

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Abstract. In line with our previous study (Eglitis R I *et al* 1998 *J. Phys.: Condens. Matter* **10** 6271) for a single Nb impurity and Nb clusters in $KTaO_3$ we present here the results of calculations for a series of perovskite $KNb_xTa_{1-x}O_3$ (KTN) solid solutions ($x = 0$, 0.125, 0.25, 0.75, and 1). The quantum chemical method of the intermediate neglect of the differential overlap (INDO) combined with the large unit cell (LUC) periodic model is used. According to the INDO calculations, Nb impurity becomes off-centre in $KTaO_3$ already at the lowest studied Nb concentration. Its off-centre displacement is in a good agreement with XAFS measurements. We compare our results with previous FP-LMTO calculations.

Perovskite-type oxides such as $KNbO_3$, $KTaO_3$ and their solid solutions $KNb_xTa_{1-x}O_3$ (KTN) have numerous technological applications [2]. As the temperature decreases, $KNbO_3$ goes through three ferroelectric phase transitions, whereas $KTaO_3$ remains in a non-polar phase down to low temperatures. However, the introduction of several percent of Nb or Li impurities brings $KTaO_3$ to the ferroelectric state [3–5]. This raises a question about the nature of the phase transition in KTN. X-ray photoelectron spectroscopy (XPS) has shown [6] that Ta ions are replaced in KTN by the Nb ions, whereas XAFS measurements [5] have additionally demonstrated that the Nb sits in an off-centre position. Its [111] displacement is 0.145 Å at 70 K, and changes by less than 20% as the temperature increases to room temperature. We are aware of the only theoretical calculation of the KTN solid solution made using an *ab initio* full-potential LMTO method [7]. In this study, the critical Nb concentration found for the off-centre Nb displacement in $KTaO_3$, responsible for the ferroelectric phase transition, was too high ($x = 0.25$), and was in contradiction with the experiment [5]. The purpose of this Letter is the calculation of the Nb off-centre [111] and [100] displacements in KTN solid solutions at a series of Nb impurity concentrations ($x = 0$, 0.125, 0.25, 0.75 and 1).

We have used the semi-empirical, quantum chemical method of the intermediate neglect of the differential overlap (INDO) [8]. The modification of the standard INDO method for ionic solids is described in detail in [9–11]. This method is based on the Hartree–Fock formalism and allows self-consistent calculations of the atomic and electronic structure of pure and defective crystals. Recently the INDO method has been used in the study of bulk solids and defects in many oxide [9–14] and semiconductor [15,16] materials. In particular, this method has been applied to the study of phase transitions and frozen phonons in pure $KNbO_3$ [17], pure and Li-doped $KTaO_3$ [18] and point defects—*F*-centres and hole polarons—in $KNbO_3$ [19–21]. More details about the INDO method and the relevant program CLUSTERD are given in references [8–11]. With the help of this code it is possible to perform both cluster and periodic-system calculations, as well as to carry out automated geometry optimization. In our KTN solid solution calculations we used a periodic model, the so-called *large unit cell* (LUC) model [22]. Its idea is to perform the electronic structure calculations for an extended unit cell

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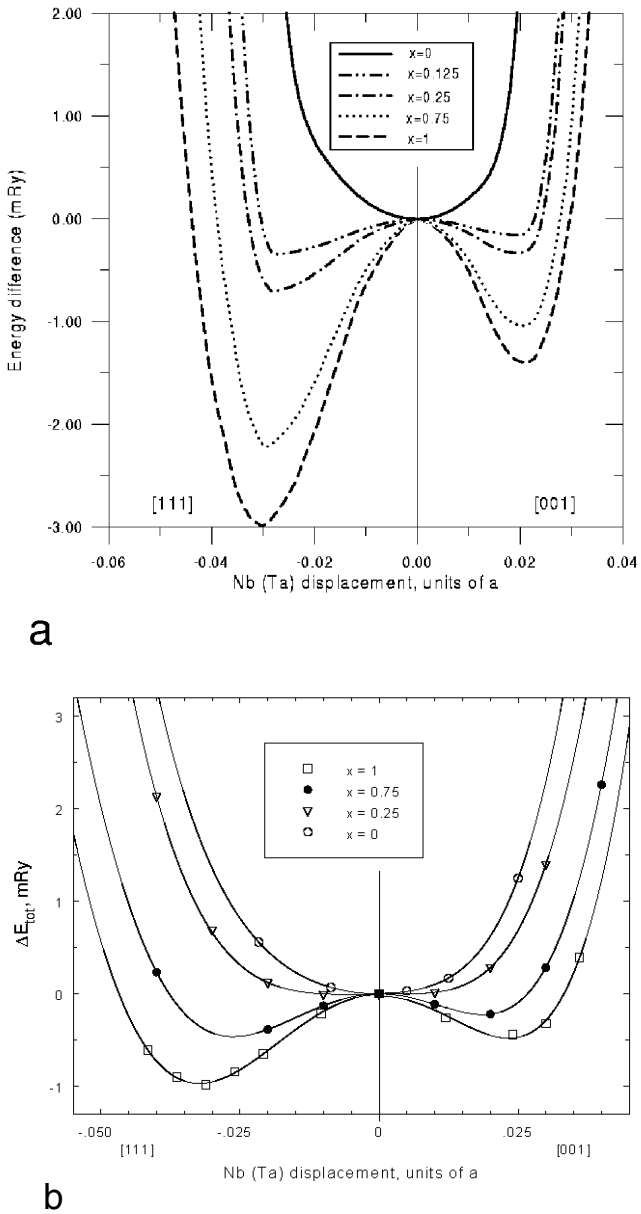

Figure 1. The total energy gain (per cell) *vs* Nb off-centre [111] and [001] displacement in $KNb_xTa_{1-x}O_3$ solid solution for Nb concentrations $x = 0$, 0.125, 0.25, 0.75 and 1, as calculated by means of INDO (a) and FP-LMTO methods [7] (b).

at the wave vector $\boldsymbol{k} = 0$ in the narrowed Brillouin zone (BZ), which is equivalent to band calculations at several special points of the normal BZ, transforming to the narrow BZ centre after the corresponding extension of the primitive unit cell. In the $KTaO_3$ case the unit cell contains five atoms, whereas the $2 \times 2 \times 2$ extended LUC used in our calculations consists of 40 atoms.

A key factor for the success of any semi-empirical method is proper parameterization. The relevant detailed analysis of the development of the INDO parametrization for pure $KNbO_3$ and $KTaO_3$ is given in [17, 18]. Note here that the INDO method reproduced surprisingly well both available experimental data and the results of *ab initio* LDA calculations. Not only the effect of a ferroelectric instability of $KNbO_3$ due to off-centre displacement of Nb atoms from the regular lattice sites but also the relative magnitudes of the relevant energy gains for the [001], [110] and [111] Nb displacements are consistent with the order of the stability of the tetragonal, orthorombic 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-centre 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 highly successful INDO parametrization has been achieved. Frozen-phonon calculations for the 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 (calculated using the Löwdin population analysis): $0.62e$ for K, $2.23e$ for Ta and $-0.95e$ for O in $KTaO_3$, which are far from those expected in the purely ionic model ($+1e$, $+5e$ and $-2e$, respectively) often used. These charges show slightly higher ionicity in $KTaO_3$ as compared with the relevant effective charges calculated for $KNbO_3$: $0.54e$ for K, $2.02e$ for Nb and $-0.85e$ for O.

Figure 1(a) shows the total energy for Nb impurity concentrations at $x = 0$, 0.125, 0.25, 0.75 and 1 in KTN as a function of its [111] and [001] off-centre displacements. First of all, a test calculation for the pure $KTaO_3$ ($x = 0$) shows no off-centre Ta displacement, in agreement with experiment. In another extreme case of pure $KNbO_3$ ($x = 1$) Nb atoms reveal very clearly the off-centre displacements along both the [111] and [001] directions. The magnitudes of these displacements are in good agreement with a recent XAFS study [23]. For three intermediate Nb concentrations ($x = 0.25, 0.5, 0.75$) our calculations give the Nb off-centre displacements which are practically independent on the impurity concentration. The calculated magnitude of 0.146 Å displacement along the [111] direction is very close to the experimental XAFS finding of 0.145 Å observed at 70 K [5]. Note that using a cluster model, we found earlier [1] that the [111] off-centre displacement of an isolated Nb in $KTaO_3$ is practically the same, 0.146 Å . Qualitatively different behaviour of Ta and Nb atoms with respect to off-centre displacements could be related to the above-mentioned higher ionicity of the Ta in a comparison with the Nb atoms. Figure 1(b) shows also results of the FP-LMTO [7] calculations in which the critical Nb concentration turns out to be much higher than experimental value.

This study demonstrates that well-parameterized semi-empirical method could serve as a useful tool for the modelling of solid solutions.

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