

Computational study of Nb doped SrTiO₃

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Abstract

A study of Nb-doping in cubic and tetragonal strontium titanate has been carried out using a developed for crystals quantum-chemical method and a periodic Large Unit Cell (LUC) model. One of the Ti atoms was substituted by Nb atom in LUC consisting of 135 atoms. The optimised geometry in the Nb-surrounding defective region showed considerable differences in atomic relaxation for two crystallographic phases. Since the Nb-doping increases the number of valence electrons by one leading to the occurrence of a local energy level within the band-gap of the crystal.

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1. Introduction

Strontium titanate (SrTiO_3) is one of the most widely used electronic ceramic materials, which has a perovskite-type structure. Its typical application is use as a grain-boundary barrier layer capacitor [1], oxygen-gas sensor [2], and epitaxial growth substrate for high temperature superconductor thin films [3] as well as catalytic material [4]. La and Nb doped SrTiO_3 not only is used as a substrate for thin-film deposition of high- T_c superconductors but also has a fundamental interest since stoichiometric SrTiO_3 is highly insulating, but a slightly reduced compound shows superconductivity.

Behaviour of the doping carriers has been long studied in the perovskites in order to understand rich variations in physical properties due to the impurity doping. The emergence of superconductivity accompanying a change of composition in the cuprates is one of the most typical examples. SrTiO_3 is known to become superconducting when a small amount of electron carriers are doped by La substitution for a Sr atom [5] and Nb substitution for a Ti atom [6]. Since SrTiO_3 crystallises at room temperature in the simple-cubic perovskite structure (lattice parameter $a = 3.9051 \text{ \AA}$) it offers a natural starting point for the study of the electronic structure of many transition-metal oxides with similar crystal structure. Many band structure calculations and experimental works, including optical reflectance spectroscopy, electron energy loss spectroscopy, ultraviolet photoemission spectroscopy and x-ray photoemission spectroscopy have been performed for the electronic structure of SrTiO_3 .

2. Method

SrTiO₃ single crystal has two phases, above 105 K it exists in cubic phase and it switches to tetragonal phase, or ferroelectric phase, below this temperature. In order to understand fully the effects of Nb doping, both phases need to be studied.

With this objective in mind we have used a quantum-chemical model based on the Molecular Orbital theory. The electronic band structure of the perfect crystal was studied using the periodic Large Unit Cell (LUC) method within the Intermediate Neglect of Differential Overlap (INDO) approximation for crystals [7], which calculates both the total energy of the perfect crystal and the electronic structure via a Linear Combination of Atomic Orbitals (LCAO). The central point of the LUC model consists in computing the electronic band structure of the unit cell extended in a special manner at $\mathbf{k} = 0$ in the reduced Brillouin zone (BZ). This is equivalent to the band structure calculation at those BZ \mathbf{k} points, which transform to the reduced BZ centre on extending the unit cell. Thus total energy of the LUC is given by the following expression:

$$E_{LUC} = \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}^{00}} + \frac{1}{2} \sum_{A \in LUC} E_C^A + \sum_j^{N_{occ}} \epsilon_j(0) + \frac{1}{2} \sum_{\nu, \mu \in LUC} \rho_{\mu\nu}(0) Q_{\mu\nu} \quad (1)$$

Here, $\epsilon_j(\mathbf{k})$ are the eigenvalues of the Fock matrix, N_{occ} is the number of the occupied electronic states in the system, $\rho_{\mu\nu}(\mathbf{k})$ are the density-matrix elements in the basis of the Bloch orbitals, and

$$E_C^A = Z_A \sum_{l \neq 0} \sum_{B \in LUC} \left[\frac{Z_B}{R_{AB}^{01}} - \sum_{\mu \in B} \rho_{\mu\mu}(0) (v^{AO})_{\mu\mu}^l \right] \quad (2)$$

$$Q_{\mu\nu} = T_{\mu\mu}^{00} - \sum_{A \in LUC} Z_A (v^{AO})_{\mu\mu}^{00} + \sum_{l \neq 0} H_{\mu\mu}^{01} \quad \text{if } \mu = \nu \quad (3)$$

$$Q_{\mu\nu} = \sum_{l \neq 0} H_{\mu\nu}^{01} \quad \text{if } \mu \neq \nu \quad (4)$$

where $T_{\mu\mu}^{00}$ are the matrix elements of the kinetic-energy operator, $(v^{AO})_{\mu\mu}$ are those of the electron-core interaction operator, R_{AB}^{01} is the distance between the cores of the atoms A and B, and Z_A and Z_B are the charges of these cores. The computer used for this study was working with a Pentium MMX processor of 200 MHz and had a RAM of 32 Mb; the code was run in DOS mode. We would like to note that the current computational scheme has been already used successfully to study a number of perovskite-type crystals. Some examples include the hole self-trapping studies in BaTiO₃ and SrTiO₃ [8-10], La-doping in SrTiO₃ [11, 12] and studies of vacancy-related defects in both surface [13, 14] and bulk [15] of SrTiO₃ crystals. The INDO parameter sets utilised in the present work were taken from Ref. [7] for O 2s and 2p AOs, Ref. [16] for Ti 3d, 4s and 4p AOs, Ref. [11] for Sr 4p and 5s AOs and Ref. [17] for Nb 5s, 5d, and 4p AOs. Thus one can see that we have used the so-called valence basis set. The parameter sets are shown in Tables 1 and 2.

3. Features of the perfect crystal

In order to reproduce the main features of pure SrTiO₃ crystal in its cubic and tetragonal phases we have studied an 8 times (2x2x2) extended primitive unit cell of 5 atoms. By means of these calculations we could reproduce the lattice parameters of the crystal, and main properties of the electronic band structure. The calculated values of $a = 3.90 \text{ \AA}$ for the cubic phase and $a = 3.88 \text{ \AA}$ and $c = 3.92 \text{ \AA}$ for the tetragonal phase were found to be in complete agreement with the experimentally known values [18]. It was found that the lower valence band (LVB) is composed of O 2s states while the UVB predominantly is O 2p in nature. The narrow subband of Sr 4p states is located just between the two valence bands. There is some alteration for the tetragonal phase where a noticeable admixture of Ti 3d states is found in the UVB and a considerable

amount of O 2p states are present in the conduction band (CB). This points out to the hybridisation between the Ti 3d and O 2p AOs, the typical effect of ferroelectricity.

4. Nb-doping

We considered the size of 40-atom LUC to be insufficient in order to avoid the interaction between the impurities. That is why the size of the LUC was increased up to 135 atoms in order to study the behaviour of the doped SrTiO₃ crystal. For this reason we extended the primitive unit cell consisting of five atoms 27 times (3x3x3). Then a Nb atom replaced one of the Ti atoms in the centre of the LUC. This doping was made for both phases of the crystal in order to find the differences or similarities between them.

As it was found, the relaxation of the atoms around the impurity in the cubic phase is completely symmetric, the Sr atoms move outward the impurity by 0.08 Å and the O atoms move toward it by 0.01 Å. Actually such an outcome was expected due to the high symmetry of the crystal.

On the other hand, the relaxation of the atoms in the tetragonal phase show, as expected, completely symmetric movements of atoms within the xy plane, but somewhat different relaxation along the ferroelectric z axis as it can be observed in Fig. 1. We think that some special attention should be paid to the fact that the motion of the atoms along this direction is not the same even for the atoms of the same kind. The movements of the oxygens are rather particular within the plane, which contains the impurity. Similar fact also was observed in the La doping [11, 12]. Besides, due to the difference between the O atoms above and below the Nb-containing plane, we think that not only the Coulomb interaction, but also the size of the impurity is important in the

distortion of the lattice. This might imply that the Nb atom also has some kind of movement. However, it is so small that our calculations simply can not take it into account, but bigger effects in the surrounding region, e.g. defect-closest atom movements can be noticed.

As it was stated above, the crystal is ferroelectric in the tetragonal phase, which means that a spontaneous electric dipole exists. This dipole might interact with a local dipole produced in the defective region. Thus one can expect that these two dipole moments would try to align. This dipole-dipole interaction could be the dynamic condition leading to the relaxation we have been able to calculate not just in this material, but also in the other titanates [8-13]. We have to point out that even though the SrTiO₃ crystal is a ferro-distortable material, we could not find any kind of rotation of the nearest O and/or Sr atoms around the ferroelectric z axis.

The analysis of the calculated electronic structure besides similarities for both phases shows a noticeable admixture of the O 2p in the conduction band and the Ti 3d AOs in the UVB for the tetragonal phase, which is a typical effect for any ferroelectric titanate [19]. Besides, we have found that in both phases of the crystal the Nb atom induces the local energy level within the band-gap close to the conduction band.

Some experiments have been made in order to observe conducting and superconducting properties in Nb-doped SrTiO₃ [6]. In those experiments it was established that the Curie temperature T_c is equal to 0.43 K. Our calculations have not shown any evidence of free electrons in the conduction band, which might be explained due to the low experimental superconducting temperatures. We can also suggest that since the Nb-induced local energy level is observed rather close to the conduction band, it would be possible that electron transfer to the conduction band occurs by the tunnelling effect.

5. Conclusions

In the present work we have studied the effects of the Nb doping in the SrTiO_3 crystal considering both, cubic and tetragonal phases. We have found that the lattice relaxation is as expected. The movements are completely symmetric in the cubic phase, while in the tetragonal phase the symmetry is broken along the ferroelectric z axis. We believe that this kind of motion in the tetragonal structure is due to a local change in the electric dipole moment and its subsequent interaction with the dipole moment of the entire crystal. Thus the presence of the Jahn-Teller effect might be neglected.

Although our calculations do not show any evidence of free electrons in the conduction band, it can be observed that one electron of the Nb atom inserted into the LUC of 135 atoms produces the local energy level within the band-gap of the crystal. Since this level is situated very close to the conduction band, it might transfer to the conduction band by the tunnelling effect, which would increase the conductivity of the crystal.

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Table 1. The INDO parameter sets used in the present work.

Atom	AO	ζ	E_{neg}	P^0	β
Sr	5s	1.59	11.15	0.18	-0.4
	4p	2.80	37.5	2.00	-4.5
Ti	4s	1.4	3.7	0.65	-0.5
	4p	1.1	-15.0	0.04	-0.5
	3d	1.93	7.2	0.55	-9.0
O	2s	2.27	4.5	1.974	-16.0
	2p	1.86	-12.6	1.96	-16.0
Nb	5s	1.55	24.5	0.8	-0.5
	5d	1.40	2.0	0.01	-0.5
	4p	1.35	23.7	0.117	-8.0

Table 2. The two-centre parameters $\alpha_{\mu\text{B}}$ (au^{-1}), the numbers in the parenthesis show the corresponding values of this parameter for the tetragonal phase.

A	B			
	Sr	Ti	O	Nb
Sr	0.15	0.55	0.25	0.00
Ti	0.09 (0.10)	0.13 (0.16)	0.10 (0.14)	0.00
O	0.59	0.38 (0.362)	0.15	0.36
Nb	0.21	0.18	0.10	0.10

Figure Captions

Fig. 1. Atomic relaxation in the tetragonal phase of 135-atomic LUC.

