A THEORETICAL STUDY OF LA-DOPING IN STRONTIUM TITANATE

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Abstract

A study of La-doping in strontium titanate cubic and tetragonal phases has been carried out by means of an advanced quantum-chemical method developed for crystal calculations. The optimized geometry in the La-surrounding defective region shows considerable differences in atomic relaxation between two crystallographic phases. Calculated defect-induced local energy levels within the band-gap are discussed in terms of the available experimental data on the superconductivity studies.

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1. Introduction

The perovskites are an extremely important class of ceramic materials. 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], epitaxial growth substrate for the high temperature superconductor thin films [3] and catalytic material [4]. $SrTiO_3$ has also been known to become superconducting when a small amount of electron carriers are doped by a La substitution for Sr atom [5].

By means of the modified for crystals Intermediate Neglect of Differential Overlap (INDO) method [6] and using the periodic Large Unit Cell (LUC) model [7], we have modeled the La doping in the cubic and tetragonal crystalline lattices of $SrTiO_3$. Our method has been successfully employed before to investigate a number of oxide crystals. In particular, the method has an important advantage of geometry predictions for crystals doped with impurity atoms. Thanks to the very precise geometry reproduction some fundamental problems concerning Li intercalation in TiO_2 crystals were successfully resolved [8, 9]. We have to note that within our method no *a priori* assumption is made about the pattern of the electronic density distribution in the vicinity of the defect under study, i.e., it is obtained in the self-consistent-field (SCF) manner. This leads to a reliable information about the defect influence upon the electronic band structure properties.

The computational method as it is implemented in the CLUSTERD computer code [10] and in particular, the LUC model has been recently used successfully in studies of perovskite-type ceramics. In particular, the modeling of phase transition in $KNbO_3$ crystal [11] and impurity-doping studies in $BaTiO_3$ crystal [12] showed the usefulness of the computer code in studies of this type of ceramics. The aim of this work is to predict the most stable structures of $SrTiO_3$:La for both phases and to study the influence of La impurity upon the band structure properties of the strontium titanate.

2. Method

The modified for crystals INDO method is based on the Molecular Orbital (MO) theory and a specific semi-empirical parametrization scheme [6] developed for crystal computations. We use a periodic supercell model based on the LUC approach. The model is free from the limitations of different cluster models, in particular, the LUC (i) takes into account explicitly the periodicity of a crystal under study, and (ii) considers completely the exchange interaction. The basic mathematical equations of the model are given in [7, 10].

The parameter set for the O atom was taken from [10] whereas the one for the Ti atom was taken from [8, 13]. A small modification in Ti parameters was made to reproduce more precisely the conduction band properties. Finally, the parameter set for the Sr atom was obtained reproducing the electronic band structure and spatial properties of the $SrTiO_3$ crystal for both, cubic and tetragonal phases, as well as the basic features of the Sr atom and the SrO molecule. Details of the parametrization are given in [12] while all semi-empirical parameters are shown in Table 1. In order to reproduce the peculiarities of the tetragonal phase we utilized slightly different numerical values for some of the two-center α parameters.

In order to study La-impurity doping, we had to obtain semi-empirical parameters for the La atom. We got these parameters by reproducing (i) the ground state of the LaO molecule $^2\Sigma^+$, (ii) the inter-atomic distance in this molecule equal to 1.825 Å, which matches exactly the experimental result [14] and finally (iii) the first two ionization potentials of the La atom (see Table 2).

3. Electronic band structure and geometry of the SrTiO3 cubic and tetragonal phases

Using the LUC of 40 atoms we have computed the electronic band structure of $SrTiO_3$ cubic and tetragonal phases. The obtained results are in a good agreement with the experimental X-ray photoelectron spectra measurements [16]. The lower valence band (LVB) is composed of O 2s states while the upper valence band (UVB) predominantly is O 2p in nature. The narrow subband of Sr 4p states is located just between two valence bands. There is some alteration for the tetragonal phase where a noticeable admixture of Ti 3d states is found in the UVB. The obtained atomic charges are q(O) = -1.37 ***e***, q(Ti) = 2.23 ***e***, q(Sr) = 1.88 ***e*** and q(O) = -1.30 ***e***, q(Ti) =

2.01 ***e***, q(Sr) = 1.89 ***e*** for the cubic and tetragonal phases, respectively. One can see the difference in charges for the Ti and O atoms while for the Sr atom they are practically identical for both types of lattice. This effect, in our mind, is due to the ferroelectricity phenomenon, which occurs in the tetragonal phase. It is known that the hybridization of O 2p and Ti 3d atomic orbitals (AOs) accompanies the phase transition, cubic ⇒ tetragonal, in the titanates. This can be also seen from different compositions of the UVB, which point out to the considerable admixture of the Ti 3d AOs in the UVB in the tetragonal phase whereas this is not the case in the cubic lattice. The occurrence of Ti 3d states in the UVB makes atomic charges on Ti atoms more negative and those on O atoms more positive in accordance with our results.

We managed to reproduce successfully the spatial characteristics of both crystallographic lattices. The obtained lattice constants were found to be equal to a_o = 3.90 Å for the cubic lattice and a_o = 3.88 Å, c_o = 3.92 Å for the tetragonal lattice, respectively. All these values coincide with the corresponding experimental magnitudes [17].

4. Lattice distortion due to the La-doping

The effects of structural phase transition in strontium titanate have attracted a great deal of attention and up to now there are some unclear points in the description of this phenomenon [18]. We have computed La-impurity inserted into the 40-atom LUC of the $SrTiO_3$ crystal in order to study the effect of impurity presence upon the crystalline lattice distortion. The La atom substituted one of the Sr atoms situated in the center of the LUC and different geometry optimization options were considered. As a result, we have found that in the cubic phase the atomic movements are completely symmetric (see Fig. 1(a)). The four La-nearest Ti atoms move outwards by 0.04 Å along the <111> directions while the La-closest O atoms move towards the La-impurity by 0.05 Å along the <110> directions (see Table 3 for more details).

The obtained lattice distortions for the tetragonal lattice are considerably different from those observed in the cubic phase. The La-nearest O atoms move symmetrically towards the impurity-atom by 0.03 Å along the <110> directions. On the other hand, the La-nearest Ti atoms move outwards by 0.08 – 0.09 Å and these displacements are asymmetric (see Table 4 and Fig. 1(b)), i.e., the displacements are considerably larger along the z direction and additionally the Ti atoms tend to rotate. We explain this effect by the ferroelectricity phenomenon, which is present in the tetragonal phase. Thus, the impurity atom can act as the center of a new phase and facilitate the phase transition. The rotations of light Ti atoms could be important in the phase transition reaction if the impurity-atom is present.

5. La atom influence upon the band structure properties

In order to explain experimental results obtained for La-doping in the superconducting phase [5], we have computed two La-impurity atoms in 160 atomic LUC for both cubic and tetragonal phases. In the case of two impurity-atoms, we have two extra electrons in the system. They can occupy the same local energy level within the band-gap forming the singlet state, and/or they can occupy two separate local energy levels leading to the triplet state. During the calculations we have obtained a local energy level situated at 2.8 eV and 1.8 eV above the top of the UVB for the singlet and triplet states, respectively. This agrees very well with the experimental data of 2.4 eV and 1.5 eV. Thus, we explain the origin of two peaks in the ultraviolet photoemission spectroscopy (UPS) measurements [5] by two different system's states: the experimental peak at 2.4 eV corresponds to the singlet state and the one located at 1.5 eV above the top of the UVB corresponds to the triplet state. By comparing total energies of the systems with different states, we have found that the triplet state is energetically more favorable than the singlet state by approximately 1.0 eV. If we repeat the same kind of computations in the 80-atom LUC, i.e., increasing La concentration twice, the favourability of the triplet state increases to 1.3 eV. This explains the experimental observation of the augmentation of intensity of the 1.5 eV peak (which is the triplet state according to our theory) with increasing La concentration. It has to be noted that this outcome was obtained only for the tetragonal phase while in the case of the cubic phase, the local energy levels for both, singlet and triplet, states are around 2.0 eV above the top of the UVB. Finally, two La atoms in the 160 atomic LUC model correspond to the following La concentration: $La_{0.0625}Sr_{0.9375}TiO_3$, this is very close to the one used in the experiment [5]: $La_{0.05}Sr_{0.95}TiO_3$.

6. Conclusions

Using the developed for crystals INDO method we have studied structural and electronic properties of La-doped $SrTiO_3$ crystal. Both known phases, cubic and tetragonal, were investigated. Comparing the obtained results for two phases we came to the following conclusions:

(i) the utilized computer code is reliable in reproducing the effects of ferroelectricity, e.g., the hybridization of O 2p and Ti 3d states;

(ii) it is important to consider Ti rotations in order to explain defect-induced lattice distortion and possibly phase transition in this material;

(iii) the origin of two local energy levels within the band-gap observed experimentally in the superconducting phase of $SrTiO_3$ is two different system states: singlet state corresponding to the case when two extra electrons occupy the same local energy level within the band-gap and triplet state when the extra electrons occupy different local one-electron levels.

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Figure captions

Fig. 1. Atomic displacements in the cube fragment projected onto the yz plane for (a) cubic and (b) tetragonal phases, respectively. The atomic displacements are symmetrical for the cubic phase and asymmetrical for the tetragonal one.

Table 1. (a) The semi-empirical parameters used in the present work. (b) The two-center parameters $\alpha_{\mu B}$ (au^{-1}), the numbers in the parenthesis show the corresponding parameters for the tetragonal phase.

(a)

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
La	6s	1.0	11.3	0.40	-0.4
	6p	1.0	2.0	0.01	-0.4
	5d	1.97	11.0	0.08	-6.3

(b)

A	B			
	Sr	Ti	O	La
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	0.53
La	0.01	0.02	0.03	0.01

Table 2. INDO calculated ionization potentials for a La atom (in eV) versus the experimental values [15].

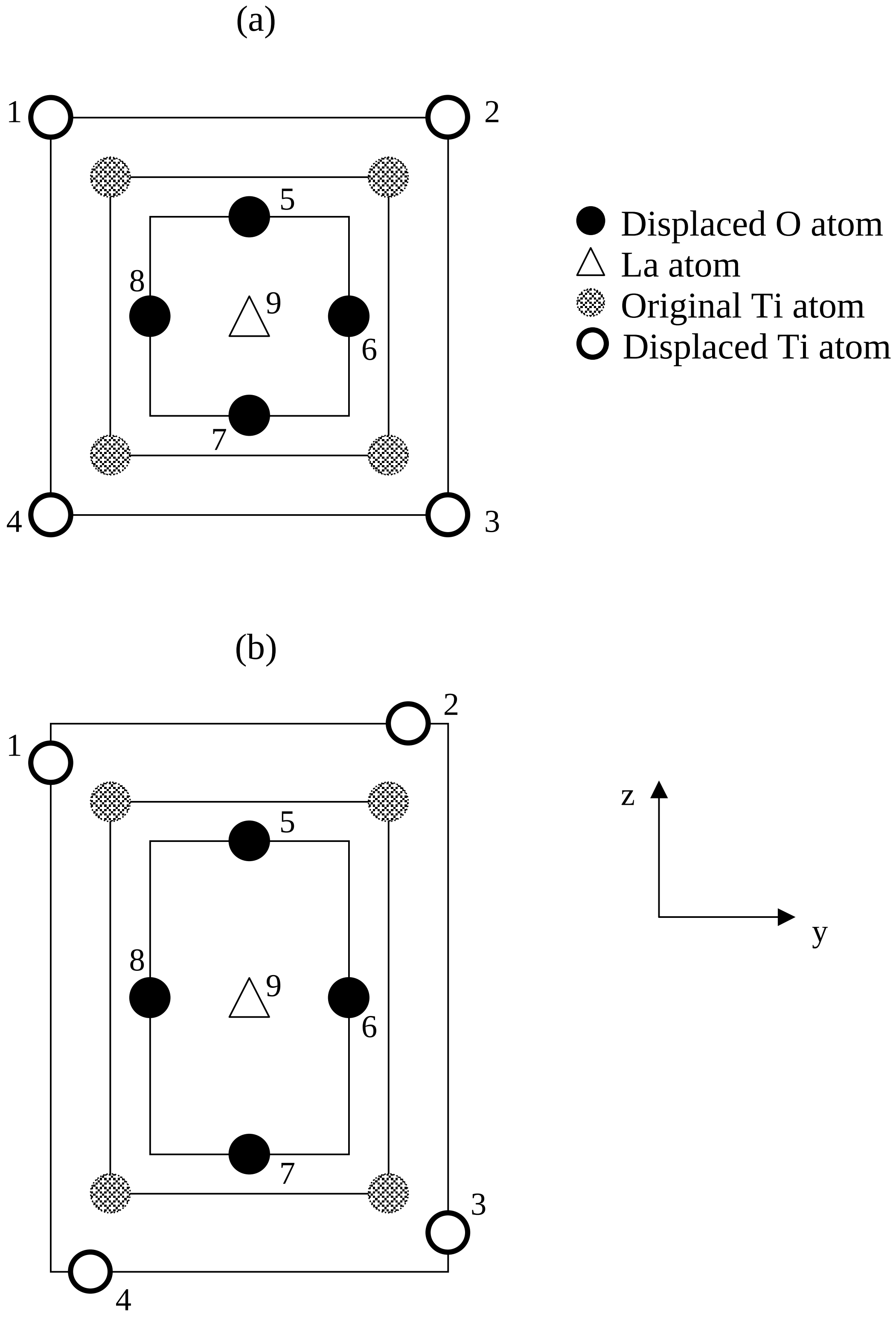
	INDO results	Exp. data
1st IP	5.64	5.61
2nd IP	11.59	11.43

Table 3. Atomic charges (in ***e***) in the perfect and La-doped $SrTiO_3$ cubic phase and atomic displacements (in Å) due to the impurity presence. The atomic numeration corresponds to the one in Fig. 1 (a).

Atom	Charge		Displacement		
	Perfect crystal	Doped crystal	x	y	z
Ti(1)	2.23	2.41	0.023	-0.023	0.023
Ti(2)	2.23	2.41	0.023	0.023	0.023
Ti(3)	2.23	2.41	0.023	0.023	-0.023
Ti(4)	2.23	2.41	0.023	-0.023	-0.023
O(5)	-1.37	-1.41	-0.038	0.000	-0.038
O(6)	-1.37	-1.41	-0.038	-0.038	0.000
O(7)	-1.37	-1.41	-0.038	0.000	0.038
O(8)	-1.37	-1.41	-0.038	0.038	0.000
La(9)	—	1.56	0.000	0.000	0.000

Table 4. Atomic charges (in ***e***) in the perfect and La-doped $SrTiO_3$ tetragonal phase, atomic displacements (in Å) and rotations (in degrees) due to the impurity presence. The atomic numeration corresponds to the one in Fig. 1 (b).

Atom	Charge		Displacement			α
	Perfect crystal	Doped crystal	x	y	z	
Ti(1)	2.01	2.18	0.038	-0.038	0.061	0.47
Ti(2)	2.01	2.18	0.038	0.023	0.076	0.56
Ti(3)	2.01	2.25	0.038	0.038	-0.061	0.53
Ti(4)	2.01	2.25	0.038	-0.023	-0.076	0.65
O(5)	-1.29	-1.32	-0.023	0.000	-0.023	
O(6)	-1.31	-1.35	-0.023	-0.023	0.000	
O(7)	-1.29	-1.39	-0.023	0.000	0.023	
O(8)	-1.31	-1.35	-0.023	0.023	0.000	
La(9)	—	1.58	0.000	0.000	0.000	


(a)
1
2
5
8
9
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● Displaced O atom
△ La atom
▨ Original Ti atom
○ Displaced Ti atom
(b)
2
1
5
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z
y