

Periodic LUC study of F centers in cubic and tetragonal SrTiO₃

Arvids Stashans*, Fernando Vargas

*Centro de Investigación en Física de la Materia Condensada, Corporación de Física
Fundamental y Aplicada, Apartado 17-12-637, Quito, Ecuador*

Abstract

Modified for crystals quantum-chemical computational approach and the periodic LUC (Large Unit Cell) model is used for calculating structural, electronic and optical properties of F centers (two electrons trapped by an oxygen vacancy). The automated geometry optimization is carried out for the ground state of defect in both cubic and tetragonal crystalline lattices of SrTiO₃. The wave functions of two extra electrons extend over the two vacancy-closest Ti atoms and over other nearby atoms. The absorption energies are calculated using the Δ SCF scheme after the performance of system's geometry optimization. The obtained results are discussed in a comparative manner for two different crystallographic phases.

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* Corresponding author. FAX: +593-2-403656.

E-mail address: sauleskalns@yahoo.com (A. Stashans).

1. Introduction

Strontium titanate (SrTiO_3) is a fascinating material, proving its usefulness in a wide range of applications. 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 as a catalytic material [4]. SrTiO_3 has also been known to become superconducting when a small amount of electron carriers are added by oxygen vacancy substitution for O, Nb substitution for Ti, and La substitution for Sr [5-7].

It is well understood that point defects play an important role in many applications of ceramic materials. One of the most common defects in oxide crystals is the so-called F center (two electrons in an oxygen vacancy). This defect can contribute to the absorption spectra of the material and is also of great theoretical interest due to the occurrence of superconductivity when an oxygen vacancy substitutes for O [5]. However, to our knowledge no theoretical attempts have been done so far to study this defect in the SrTiO_3 crystal.

In this paper, the electronic structure of SrTiO_3 crystal having F center is studied using the Hartree-Fock (HF) semi-empirical CLUSTERD computer code [8]. This computer program is specially designed for periodic system, e.g., crystal calculations. Due to its semi-empirical character, the method is not cumbersome and time consuming in the treatment of the electronic and spatial structure of complex systems, especially with partially covalent chemical bonding, like oxide crystals. We have to note that, within our method, no *a priori* assumption is made upon 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 permits us to get reliable information about the

defect influence upon the electronic band structure properties. The method allows one to calculate with reasonable precision the excited state of the system, thus giving one the information about defect contribution to the absorption spectra of the crystal (Δ SCF method).

The method has been already applied to F center studies. In particular, the ground and excited state calculations of F-type centers in corundum (α - Al_2O_3) crystal [9, 10] gave some important answers on contradicting experimental data. The method also has been used in the investigation of F centers in KNbO_3 crystal [11], which has structural similarity to the strontium titanate. We have applied the CLUSTERD computer code to study SrTiO_3 and point defects therein before. The investigation of La-doping in SrTiO_3 [12-14] led us to the explanation of the origin of two peaks in the band-gap region of the superconducting SrTiO_3 found recently by the photoemission spectroscopy measurements [15]. Additionally, we have successfully used this method in studies of point defects in another titanates like BaTiO_3 [16] and CaTiO_3 [17].

The aim of this work is to obtain the lattice distortion due to the F center presence in both cubic and tetragonal crystalline lattices of SrTiO_3 . We also calculate absorption energies of F center in both phases. The analysis of F center influence upon different properties of the crystal is given in a comparative way for two structures: cubic *versus* tetragonal.

2. Computational method

A version of the Intermediate Neglect of Differential Overlap (INDO) method, modified for crystal calculations, is used in the present work. This technique is based on the MO theory and a specific parametrization scheme [18] developed for crystal, i.e.,

periodic system, studies. The numerical parameter set for a particular chemical element is optimized to match the main experimental features of the studied crystal: electronic band structure, the effective charges on the atoms, and structural parameters, as well as the basic properties of some selected test molecules, e.g., equilibrium distance between the atoms in the molecule and ionization potentials. The parameter sets used in our work are taken from [8] for O and [16] for Ti atoms. The details of the SrTiO₃ crystal parametrization and Sr parameter set are described in [12].

The periodic Large Unit Cell (LUC) model is used in the present computations. It has to be noted that the periodic LUC model considers the electronic band structure and calculates the total energy of the system very accurately, due to not only the periodicity condition but also a careful treatment of exchange interaction. A full account of the method used to calculate the total energy of the crystal within the LUC framework is found in [19].

In our case, a 40-atom LUC (supercell) was considered to study F centers in cubic and tetragonal lattices of SrTiO₃, i.e., we used an 8-fold-symmetric extension of the strontium titanate primitive unit cell. As indicated by numerous computations [8, 11, 16], an 8-fold or even 4-fold-symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic density distribution in the crystal.

3. F centers in cubic lattice of SrTiO₃

One of the oxygens situated in the middle of the LUC was taken out of the system and two electrons were inserted instead. As a result we have the following lattice distortion (see Fig. 1). Two Ti atoms situated along the z axis move outwards from the

F center by 0.09 Å and 0.08 Å, respectively. The four Sr atoms in the xy plane also move outwards from the defect along the $\langle 110 \rangle$ directions by 0.05 Å each. Finally, eight O atoms also tend to move away from the center of the system occupied by the F center by 0.02 Å each. The final atomic configuration obtained using the automated geometry optimization procedure thus shows us symmetric displacements of O and Sr atoms and only slightly asymmetric movements of two defect-closest Ti atoms. Thus obtained relaxation energy E_{rel} is equal to 1.72 eV.

The two inserted electrons are well localized within the two vacancy-nearest Ti atoms. As it follows from our outcome, two vacancy-closest Ti atoms share 85% of the wave function almost evenly.

4. F centers in tetragonal lattice of SrTO₃

As in the cubic phase, two electrons were introduced into the LUC instead of an O ion. The automated geometry optimization of the system led us to a pattern of atomic displacements similar to that of the cubic lattice (see Table 1). However, the magnitudes of atomic movements are larger compared to those of the cubic phase. We explain this effect by stronger perturbation, which is produced by the same point defect in a more compact crystalline lattice, leading to a larger lattice distortion. The asymmetry, e.g., bigger displacements along the ferroelectric z axis, is observed in the tetragonal structure. Obviously, this effect is the property of the lattice having tetragonal symmetry. The calculated relaxation energy is found to be equal to 1.17 eV.

Compared to the case of the cubic phase the wave functions of the two inserted electrons are considerably more extended in the space. The electronic charge redistributes almost equally among all Ti atoms, which enter the LUC. Still, the main

part of the electronic density of the two extra electrons is found on the two defect-closest Ti atoms. This seems to point out to the occurrence of free electrons in the conduction band, i.e., the F centers do not normally form in this case. The augmentation of number of free electrons in the conduction band also is in direct relation with the observed superconductivity phenomenon in the tetragonal phase [5].

5. Optical properties

The absorption energies were obtained as a difference of total energies for the SCF ground and excited states for optimized defect geometry (Δ SCF method). That is, the potential-energy curves are calculated for the ground and excited states of defect. Then, according to the Frank-Condon principle, the absorption energy is equal to the energy difference between the two levels corresponding to the relaxed ground state and the SCF excited state for a fixed atomic configuration. Note that these Δ SCF energies do not coincide with just the difference of the relevant one-electron energies, which usually give only rough estimates for the absorption energies. Thus obtained absorption energies are equal to 1.69 eV and 0.85 eV for the F center in the cubic and tetragonal phases, respectively. We have to note that in the tetragonal structure we encountered difficulties in obtaining reasonable precision for the excited-state SCF procedure.

6. Conclusions

F centers (two electrons in an O vacancy) are studied theoretically for the first time in the SrTiO₃ crystal, using the advanced quantum-chemical method developed for crystal computations. The defect influence upon structural, electronic and optical

properties of the material is investigated in the comparative manner for cubic *versus* tetragonal lattices. The main conclusions are as follow:

- (i) defect-produced perturbation on the tetragonal phase structure is stronger than in the case of the cubic lattice; this leads to larger lattice distortion in the latter case;
- (ii) F center wave function is well localized within the two nearest Ti atoms in the cubic phase while it is very extended in the case of the tetragonal lattice, which leads us to the conclusion that electrons are not well trapped by the O vacancy. They tend to become free, conductive electrons in the tetragonal structure.

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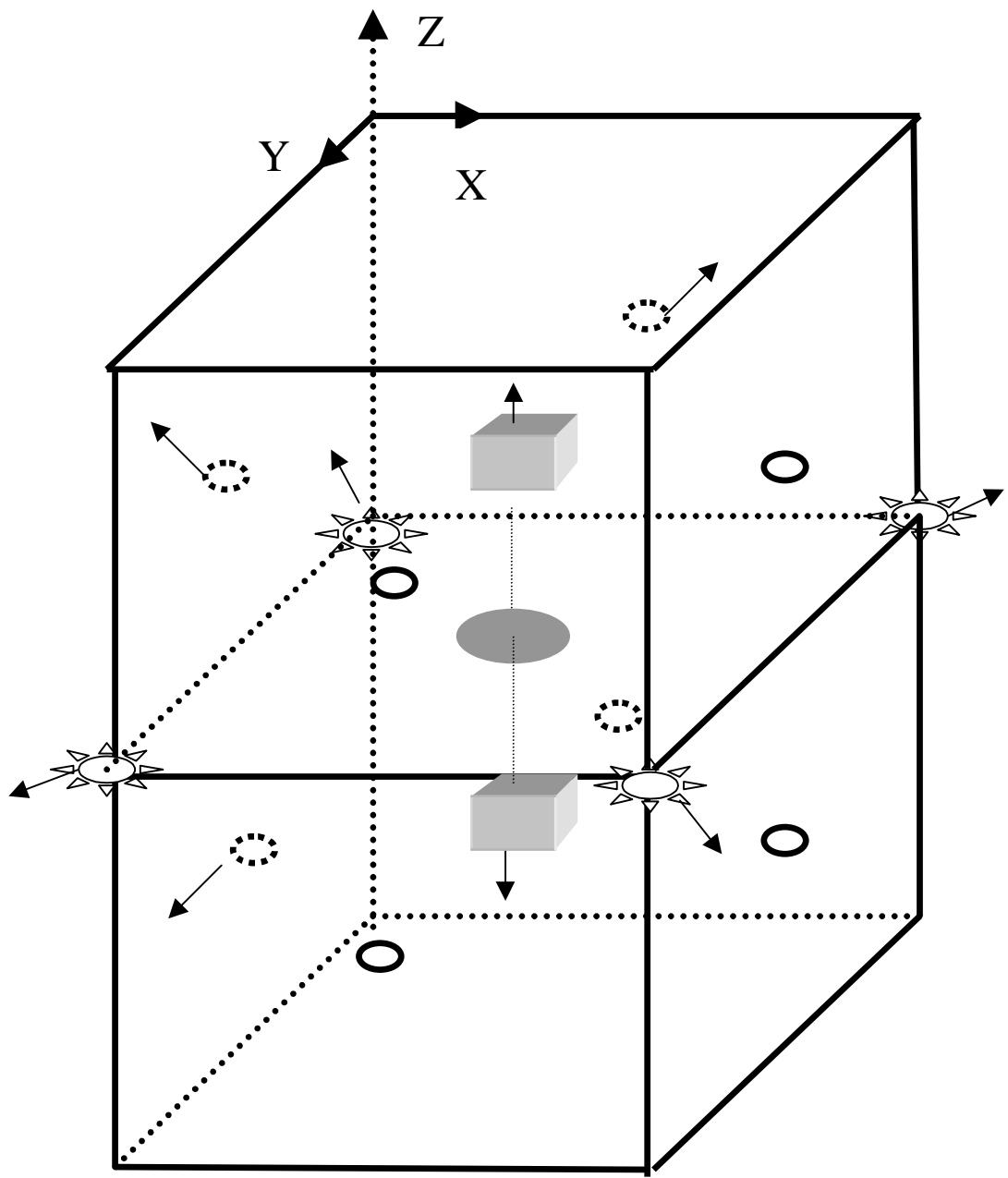
Table 1

Atomic displacements (in Å), lattice relaxation energies (in eV) and absorption energies (in eV) due to the F centers in cubic and tetragonal lattices of SrTiO₃ crystal.

Feature	Cubic system	Tetragonal system
Ti displacements	0.08-0.09	0.10-0.27
Sr displacements	0.05	0.07
O displacements	0.02	0.15-0.20
Relaxation energy	1.72	1.17
Absorption energy	1.69	0.85

Figure captions

Fig. 1. The lattice distortion in the SrTiO_3 crystal due to the presence of F center. The defect-nearest atoms (14 in total) move outwards from the F center. These displacements are asymmetric in the case of the tetragonal lattice, i.e., we observe larger movements along the z axis.



Ti atom



Sr atom



O atom in front



O vacancy



O atom in background