



## Oxygen-vacancy defects on the SrTiO<sub>3</sub>(001) surface: a quantum-chemical study

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### ABSTRACT

A quantum-chemical study of the technologically important SrTiO<sub>3</sub>(001) non-polar surface and of O-vacancy defects therein is reported in the present work. The computations are made using a method developed for periodic systems (crystals), which is based on the Hartree–Fock theory. The atomic rearrangement due to the surface creation is obtained for pure SrTiO<sub>3</sub> by means of the periodic large-unit-cell model and uses an automated geometry optimization procedure. The same technique is employed to study the electronic, structural and optical properties of the material due to the presence of the O vacancy and F centre (two electrons in an O vacancy). The computations are carried out for both cubic and tetragonal lattices. The results obtained are discussed in terms of the available experimental data.

### §1. INTRODUCTION

The properties of metal oxides are as wide ranging as those of any class of materials. One of the most important classes of metal oxides is titanates with the perovskite-type structure. The common formula of these compounds is ATiO<sub>3</sub>, where A = Ba, Ca, Sr or Pb. Strontium titanate (SrTiO<sub>3</sub>) is a widely utilized electronic ceramic material. Its typical application is use as a grain-boundary barrier layer capacitor (Yamaoka *et al.* 1983, Fujimoto and Kingery 1985), O<sub>2</sub>-gas sensor (Gerblinger and Meixner 1991) and epitaxial growth substrate for high-temperature superconductor (HTSC) thin films (Kawai *et al.* 1991) as well as catalytic material (Mavroides *et al.* 1976).

Among the transition-metal oxides, the surface properties of SrTiO<sub>3</sub> have been extensively studied by a number of groups, motivated to a large extent by its application to the thin films of various HTSCs. Surface O vacancies in SrTiO<sub>3</sub> play a central role in the nucleation of crystal growth (Ferrer and Somorjai 1980, Aiura *et al.* 1994). Therefore, in order to improve the quality of HTSC thin films, it is necessary and important to investigate the effect of surface O vacancies on the electronic and structural properties of the SrTiO<sub>3</sub> surfaces.

SrTiO<sub>3</sub> has also attracted much attention owing to some unexplained effects. For instance, the phenomenological theory of Landau (1937) fails to explain satisfacto-

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rily the structural phase transition in SrTiO<sub>3</sub>, which demonstrates the important role of the critical fluctuations close to the transition temperature (Cowley 1996). The understanding of superconductivity in the ceramic materials has also not yet been achieved. The SrTiO<sub>3</sub> crystal has been found to become superconducting when a small amount of electron carriers are introduced by an O vacancy (Schooley *et al.* 1964), Nb substitution for Ti (Hulm *et al.* 1970), or La substitution for Sr (Suzuki *et al.* 1996). Although the surface electronic structure of transition-metal oxides is an interesting problem academically and technologically, the surface effect on the electronic structure of doped carriers has not been thoroughly discussed so far. There is a possibility that the surface electronic structure differs from the bulk structure owing to the weaker charge screening effect at the surface and the change in the electron–lattice coupling modified by the surface reconstruction (Ravikumar *et al.* 1995). Therefore, the study of F centres (two electrons in an O vacancy) could elucidate the behaviour of the electron centres and their influence upon different properties of the SrTiO<sub>3</sub> crystal.

In recent years, many studies on different crystals have been made using *ab initio* methods. However, they are not always suitable for very large systems. This is the reason why we have chosen to use the intermediate neglect of differential overlap approach developed especially for periodic systems, for example crystal studies. Our method as implemented into the CLUSTERD computer code (Stefanovich *et al.* 1990) is based on a strict and reliable parametrization scheme (Shluger 1985). This technique has its origin in a molecular orbital (MO) theory and has been found to be very reliable in the treatment of the electronic and spatial structure of perfect and defective crystals. Some examples include investigation of exciton self-trapping and Frenkel-defect pair creation in the SiO<sub>2</sub> crystal (Shluger and Stefanovich 1990), studies of hole polarons (Jacobs and Kotomin 1992, Jacobs *et al.* 1992) and their motion (Jacobs *et al.* 1993) in the corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) crystal, investigation of ground and excited states of F-type and F<sub>2</sub>-type complexes in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Stashans *et al.* 1994, Kotomin *et al.* 1995), Li intercalation studies in a TiO<sub>2</sub> crystal (Stashans *et al.* 1996a, Lunell *et al.* 1997) and the equilibrium position detection for hydrogen impurities in the WO<sub>3</sub> crystal (Stashans and Lunell 1996).

The suitability of a method for the elucidation of the electronic structure of a system depends to a large degree on the target. In this paper, the emphasis is on the computation of the SrTiO<sub>3</sub>(001) surface. A more direct and better way to achieve this would be by a unit-cell method, which accounts for translational invariance of a periodic system. Therefore, we have chosen to exploit a large-unit-cell (LUC) model with an enlarged unit cell of up to 135 atoms. We would like to note that our model has already been applied successfully for surface studies of different crystals. Some examples include the study of the charge and potential distributions near the GaP(100) surface (Stefanovich and Shluger 1994), OH<sup>-</sup> adsorption on the perfect (TiO<sub>2</sub>)(001) rutile surface (Stashans *et al.* 1996b), and also calculation of organic adsorbates on the rutile (110) surface (Persson *et al.* 1998, Patthey *et al.* 1999).

## §2. COMPUTATIONAL METHOD

The computer program utilized is based on the MO theory. It also uses some numerical parameters to approximate a number of two-centre integrals and thus to reduce considerably the computational time. The semiempirical 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

the lattice constants, as well as the basic properties of some selected test molecules, for example the equilibrium distance between the atoms in the molecule and the ionization potentials. The parametrization of the SrTiO<sub>3</sub> crystal for both cubic and tetragonal crystalline lattices have been carried out by one of the present authors and a co-worker previously in studies of La doping in this material (Stashans and Sánchez 2000). Briefly, we reproduced successfully band structure properties in accordance with X-ray photoemission spectra measurements (Pertosa and Michel-Calendini 1978) as well as some basic properties of the Sr-containing molecules.

The LUC model utilized considers the electronic band structure and calculates the total energy of the system very accurately owing to not only the periodicity condition but also a careful treatment of the exchange interaction. This is very important since the SrTiO<sub>3</sub> crystal has considerable covalency effects in the chemical bonding, which have to be taken into account to obtain a reliable outcome. A full account of the method used to calculate the total energy of the crystal within the LUC framework has been given by Evarestov *et al.* (1978) and Stefanovich *et al.* (1990). We shall therefore restrict ourselves to the most important features of the LUC approach. The basic idea of the method consists in computing the electronic band structure of the unit cell extended in a special manner at  $\mathbf{k} = \mathbf{0}$  in the reduced Brillouin zone (BZ). This is equivalent to a band structure calculation at those BZ  $\mathbf{k}$  points, which transform to the reduced BZ centre on extending the primitive unit cell. The total energy of the LUC is obtained as follows:

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

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

$$E_C^A = Z_A \sum_{l \neq 0} \sum_{B \in \text{LUC}} \left( \frac{Z_B}{R_{AB}^{0l}} - \sum_{\mu \in B} \rho_{\mu\mu}(0) (v^{A0})_{\mu\mu}^{ll} \right), \quad (2)$$

$$Q_{\mu\nu} = \begin{cases} T_{\mu\mu}^{00} - \sum_{A \in \text{LUC}} Z_A (v^{A0})_{\mu\mu}^{00} + \sum_{l \neq 0} H_{\mu\mu}^{0l}, & \text{if } \mu = \nu, \\ \sum_{l \neq 0} H_{\mu\nu}^{0l}, & \text{if } \mu \neq \nu. \end{cases} \quad (3)$$

$$\quad (4)$$

Here  $T_{\mu\mu}^{00}$  are the matrix elements of the kinetic energy operator,  $(v^{A0})_{\mu\mu}^{ll}$  are those of the electron-core interaction operator,  $R_{AB}^{0l}$  is the distance between the cores of atoms A and B, and  $Z_A$  and  $Z_B$  are charges of these cores. The Coulomb interaction is treated quite well in the LUC model because of the theory of special  $\mathbf{k}$  points (Evarestov 1982). The Coulomb lattice sums are calculated using the Ewald method (Born and Huang 1954). The exchange interaction is computed after introducing the so-called 'cut-off' function (Smith *et al.* 1985).

The numerical parameters for the SrTiO<sub>3</sub> crystal have been obtained before reproducing the most important properties of this material and also in studies of other crystals. In particular, parameters for the O 2s and 2p atomic orbitals (AOs) are taken from the work of Stefanovich *et al.* (1990), for the Ti 4s, 4p and 3d AOs and for the Sr 5s and 4p AOs from the work of Stashans and Sánchez (2000). As can

Table 1. Semiempirical parameter sets used in the present work:  $\zeta$ ,  $E_{\text{neg}}$ ,  $P^0$  and  $\beta$ .

Atom	AO	$\zeta$ (au)	$E_{\text{neg}}$ (eV)	$P^0$ (electrons)	$\beta$ (eV)
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

Table 2. Two-centre parameters  $\alpha_{\mu\text{B}}$ . The numbers in parentheses show the corresponding values of this parameter for the tetragonal phase.

A	$\alpha_{\mu\text{B}}$ (au <sup>-1</sup> )		
	B = Sr	B = Ti	B = O
Sr	0.15	0.55	0.25
Ti	0.09 (0.10)	0.13 (0.16)	0.10 (0.14)
O	0.59	0.38 (0.362)	0.15

be seen, we have restricted ourselves to the use of the valence basis set. The parameters utilized are given in tables 1 and 2.

We would like to note that the current computational method has already been applied to titanates, giving encouraging results. In particular, we have studied Nb doping in the cubic and orthorhombic phases of the CaTiO<sub>3</sub> crystal (Erazo and Stashans 2000), hole polarons and impurity centres in the BaTiO<sub>3</sub> crystal (Pinto and Stashans 2000, Pinto *et al.* 2000, Stashans and Pinto 2000) as well as point-defect studies in the SrTiO<sub>3</sub> crystal (Stashans and Sánchez 2000, Stashans 2001, Stashans and Vargas 2001).

### §3. RESULTS AND DISCUSSION

There have been several calculations of the band structure of the SrTiO<sub>3</sub> surfaces (Tsukada *et al.* 1980, Vanderbilt 1990, Kimura *et al.* 1995) using different approaches. We have chosen to use the periodic LUC model within the Hartree–Fock MO theory because of its availability for extended systems, reliability in point-defect studies and high accuracy of the method in determination of the excited state of a system.

As demonstrated by numerous computations (Stashans *et al.* 1996a, Stashans and Kitamura 1997, Stashans and Sánchez 2000), an eightfold or even fourfold symmetric extension of the primitive unit cell proves to be completely sufficient to reproduce correctly the electronic density distribution of the crystal bulk or surface. Hence we have chosen to exploit the 40-atom LUC, which corresponds to the eightfold ( $2 \times 2 \times 2$ ) extension of the primitive five-atom unit cell, for pure surface calculations. In order to study O vacancies and F centres on the SrTiO<sub>3</sub>(001) surface we constructed LUCs consisting of 135 atoms. This corresponds to the twentyseven-

fold ( $3 \times 3 \times 3$ ) symmetrically extended primitive unit cell of this material. The large size of the LUC for defect computations was chosen to eliminate any possible mutual defect–defect interactions, that is to allow the study of a *single point defect* within the periodic model.

### 3.1. Properties of a pure SrTiO<sub>3</sub>(001) surface

In order to characterize the perfect SrTiO<sub>3</sub>(001) surface, a LUC of 40 atoms was chosen and the equilibrium geometry was calculated allowing all atoms to relax in the direction perpendicular to the surface.

In the cubic phase of the material we obtained downward displacements of the atoms placed in the exterior Sr–O and Ti–O<sub>2</sub> layers by 0.06 Å each. In the tetragonal phase the atoms of the exterior Sr–O layer were also found to move downwards by 0.03 Å. However, in the case of the exterior Ti–O<sub>2</sub> layer we observed a somewhat different pattern for the atomic movements. While the O atoms of this layer tended to move downwards by around 0.04 Å, the Ti atoms of the same layer were found to move upwards, that is away from the material bulk by the same magnitude. In our mind, the displacements of Ti atoms situated in the topmost plane of the tetragonal phase might be explained by the presence of ferroelectricity. The ferroelectricity occurs owing to the displacements of Ti atoms along the  $z$  axis or the ferroelectric  $c$  axis and this is what we see in our outcome. This effect also might be attributed to the partial covalent character in the Ti–O bond (Jung 1996), which is especially evident in the tetragonal phase of the material. In general, we can note that surface creation effect upon the atomic rearrangement of the material is not very large in our case and it is normal since the (001) surface is non-polar.

The exploration of a pure SrTiO<sub>3</sub>(001) surface is important if one considers the electronic properties of this material. The straightest effect is the optical bandgap reduction due to the surface. We calculated the corresponding values of the bandgap width for both phases as a difference between the total energies for the self-consistent field (SCF) ground and excited states, denoted  $\Delta\text{SCF}$ , which corresponds to an electron excitation from the highest occupied MO to the lowest energy level in the conduction band. Thus obtained energies by the  $\Delta\text{SCF}$  method do not coincide with the difference between the relevant one-electron energies, which usually gives only a rough estimation for the optical bandgap width. The bandgap width magnitudes obtained thereby were found to be equal to 4.2 and 4.1 eV for the cubic and tetragonal phases respectively. This is somewhat less than in the case of the bulk SrTiO<sub>3</sub> calculations (Stashans 2001), where we found values of 4.5 and 4.4 eV for the cubic and tetragonal phases respectively. As can be seen, our bandgap values are considerably larger than the experimental value (Gandy 1959) of 3.2 eV. Overestimation of the bandgap width originates from neglecting the effect of the long-range electron correlation, which is a common fault of methods based on the Hartree–Fock theory. However, one can observe the tendency of bandgap narrowing due to the surface creation.

### 3.2. Oxygen vacancies

In order to investigate oxygen vacancies on the SrTiO<sub>3</sub>(001) surfaces and their influence upon different material properties we made use of a 135-atom LUC taking out one O ion, that is creating a vacancy V<sub>O</sub>. SrTiO<sub>3</sub> consists of successive Ti–O<sub>2</sub> and Sr–O planes; so two kinds of (001) surface are possible: firstly, a Sr–O surface and,

secondly, a Ti–O<sub>2</sub> surface. That is why we studied V<sub>O</sub> on these two different surfaces and also considered two different crystallographic phases: cubic and tetragonal.

The case of V<sub>O</sub> situated on the Sr–O surface of the cubic SrTiO<sub>3</sub> structure is depicted in figure 1. Here V<sub>O</sub> is surrounded by four Sr atoms in the same layer at initial distance equal to 2.71 Å. Additionally, there is one Ti atom at the distance of 1.86 Å and four O atoms at a distance of 2.67 Å belonging to the layer composed of Ti and O atoms next to the surface. We have attempted to reach equilibrium of the system by applying different relaxation modes, including the automated geometry optimization procedure (Press *et al.* 1986). As a result we have found that the atoms relax according to the Coulomb electrostatic interaction law. The positively charged Ti and Sr atoms move outwards from the positively charged V<sub>O</sub> by 0.03 and 0.07 Å respectively. These displacements are symmetrical, that is the Ti atom moves along the ⟨001⟩ direction while the Sr atoms relax along the ⟨110⟩ directions. The negatively charged O atoms move towards the V<sub>O</sub> by 0.06 Å along the ⟨101⟩ directions. The relaxation energy calculated as a difference between the relaxed and unrelaxed crystal states is found to be equal to 2.11 eV.

The case of V<sub>O</sub> on the Sr–O surface of the tetragonal SrTiO<sub>3</sub> structure (figure 2) is similar to the previous case, for example the V<sub>O</sub> has the same surroundings. We also observe similar lattice distortion due to the presence of V<sub>O</sub> on the topmost layer. In particular, the positive Sr and Ti atoms move outwards while the negative O atoms move towards the defect. However, movements of the four Sr atoms closest to the defect are along the ⟨111⟩ directions. This means that we have a *z* component for movements of the Sr atoms, which are located in the same layer as the V<sub>O</sub>. The relaxation energy obtained for this case is equal to 1.40 eV.

The case of V<sub>O</sub> on the Ti–O<sub>2</sub> surface of the cubic SrTiO<sub>3</sub> structure is shown in figure 3. Here we have the following situation. The V<sub>O</sub> has two Ti atoms at a distance

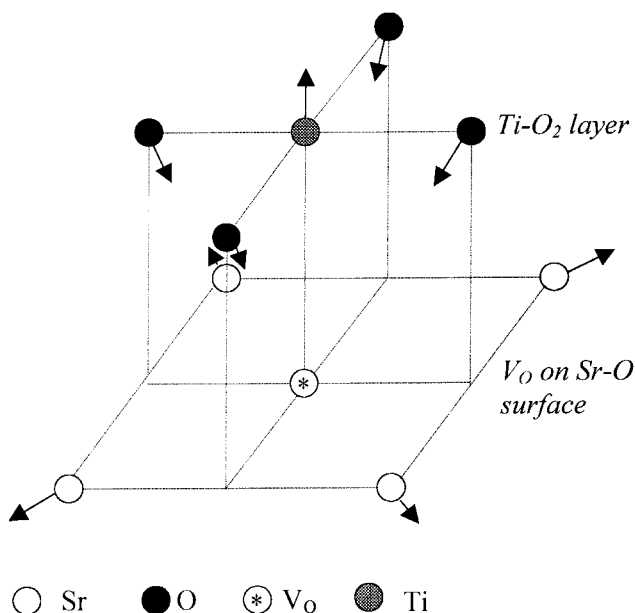


Figure 1. Atomic relaxation around the V<sub>O</sub> situated in the Sr–O layer of the cubic phase of SrTiO<sub>3</sub>.

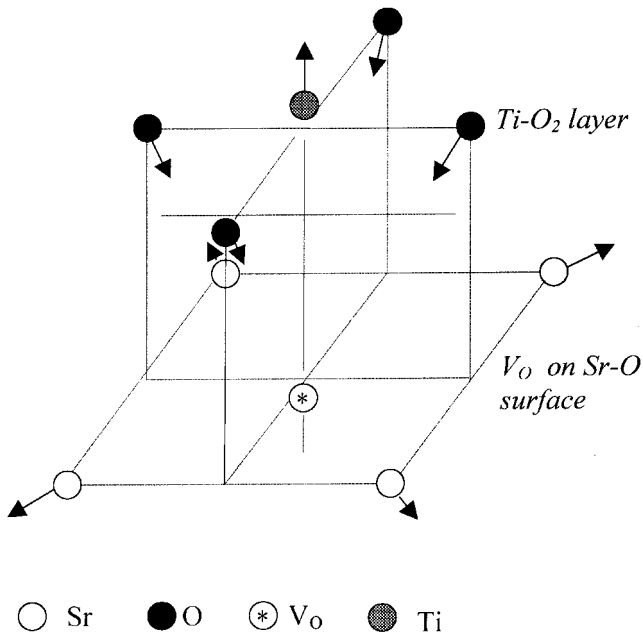


Figure 2. Atomic relaxation around the  $V_O$  situated in the Sr-O layer of the tetragonal phase of  $\text{SrTiO}_3$ .

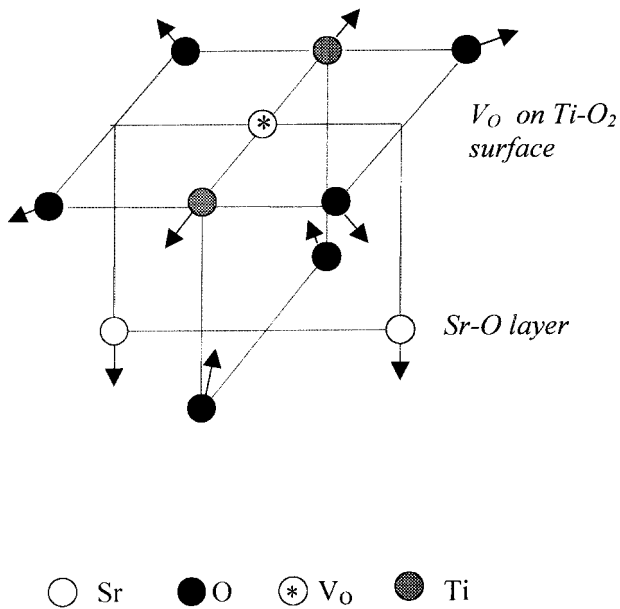


Figure 3. Atomic relaxation around the  $V_O$  situated in the  $\text{Ti-O}_2$  layer of the cubic phase of  $\text{SrTiO}_3$ .

equal to 1.92 Å and four O atoms at a distance equal to 2.71 Å situated in the same atomic layer. Additionally, there are two O atoms and two Sr atoms all at a distance of 2.67 Å, placed in the layer which is next to the surface and which is composed of Sr and O atoms. The atomic movements again can be inferred from the Coulomb interaction of a positively charged defect centre with its neighbouring atoms. In particular, the Sr and Ti atoms move outwards from the defect by 0.07 and 0.16 Å respectively. These movements are along the  $\langle 100 \rangle$  and  $\langle 101 \rangle$  directions for the Ti and Sr atoms respectively. The O atoms move towards the positively charged defect as shown in figure 3. The relaxation energy obtained for the lattice distortion around the  $V_O$  is found to be equal to 2.00 eV.

We have attempted to study the  $V_O$  on the Ti–O<sub>2</sub> surface of the tetragonal phase but did not achieve the convergence required. It is possible therefore that the surface turns out to be unstable owing to presence of the  $V_O$  or that considerable rearrangement or reconstruction is necessary to stabilize it. This is also in accordance with the experimental ultrahigh-vacuum annealing studies (Nishimura *et al.* 1999) of the SrTiO<sub>3</sub>(001) surfaces where it was found that the Sr–O bonding on the topmost SrO plane is more stable than Ti–O bonding on the Ti–O<sub>2</sub> topmost layer. The summarized results of atomic displacements around the  $V_O$  are given in table 3.

### 3.3. *F* centres

As follows from ultraviolet photoelectron spectroscopy observations (Kimura *et al.* 1995) a shallow level appears in the bandgap due to surface O-vacancy defects on the SrTiO<sub>3</sub>(001) reduced surface. Since this level is occupied, it might be attributed to the presence of an F centre. Two electrons were added to the system containing  $V_O$  to study F centres and their influence upon the structural, electronic and optical properties of this material. Similarly as for the  $V_O$ , we computed this point defect for three cases: firstly, the F centre on the Sr–O surface of the cubic structure; secondly, the F centre on the Ti–O<sub>2</sub> surface of the cubic structure; finally, the F centre on the Sr–O surface of the tetragonal structure. The summarized results of atomic displacements around the F centre for all three cases are given in table 4.

Table 3. Atomic displacements around  $V_O$  situated on the SrTiO<sub>3</sub>(001) surface. The + and – signs denote outward and inward atomic movements respectively with respect to the  $V_O$ .

Type of surface	Phase	Type of atom	Initial distance to $V_O$ (Å)	Direction of the movement	Magnitude of the movement (Å)
Sr–O	Cubic	Ti	1.86	$\langle 001 \rangle$	+0.03
		O	2.67	$\langle 101 \rangle$	–0.06
		Sr	2.71	$\langle 110 \rangle$	+0.07
Sr–O	Tetragonal	Ti	1.89	$\langle 001 \rangle$	+0.03
		O	2.59	$\langle 101 \rangle$	–0.06
		Sr	2.70	$\langle 111 \rangle$	+0.09
Ti–O <sub>2</sub>	Cubic	Ti	1.92	$\langle 100 \rangle$	+0.16
		O	2.67	$\langle 101 \rangle$	–0.14
		O	2.71	$\langle 110 \rangle$	–0.11
		Sr	2.67	$\langle 101 \rangle$	+0.07



Table 4. Atomic displacements around the F centre situated on the SrTiO<sub>3</sub>(001) surface. The + and - signs denote outward and inward atomic movements respectively with respect to the F centre.

Type of surface	Phase	Type of atom	Initial distance to V <sub>O</sub> (Å)	Direction of the movement	Magnitude of the movement (Å)
Sr-O	Cubic	Ti	1.86	$\langle 001 \rangle$	+0.08
		O	2.67	$\langle 101 \rangle$	-0.14
		Sr	2.71	$\langle 110 \rangle$	+0.14
Sr-O	Tetragonal	Ti	1.89	$\langle 001 \rangle$	+0.05
		O	2.59	$\langle 101 \rangle$	+0.08
		Sr	2.70	$\langle 111 \rangle$	+0.15
Ti-O <sub>2</sub>	Cubic	Ti	1.92	$\langle 100 \rangle$	+0.05
		O	2.67	$\langle 101 \rangle$	+0.02
		O	2.71	$\langle 110 \rangle$	-0.04
		Sr	2.67	$\langle 101 \rangle$	+0.07

Studies of the F centre on the Sr-O surface of the cubic SrTiO<sub>3</sub> show the following pattern of the atomic displacements. The Ti atom closest to the defect and the four Sr atoms surrounding the Ti atom move outwards from the F centre by 0.08 and 0.14 Å respectively. The negatively charged O atoms move towards the F centre by 0.14 Å. As one can observe these movements are similar to those in the case of the V<sub>O</sub> but they are larger in magnitude. The calculated relaxation energy for this case is equal to 2.67 eV. The two extra electrons are found localized on the four nearest Sr atoms (table 5) situated on the surface.

The atomic displacements around the F centre on the Sr-O surface but for the tetragonal phase give a somewhat different picture. While the positively charged Ti and Sr atoms move outwards from the defect by 0.05 and 0.15 Å respectively, one can also notice outward movements of the four O atoms nearest to the defect by 0.08 Å. The wavefunction of the two extra electrons is found mainly on the closest Ti atom, which is situated on the layer next to the surface. In our mind, the unexpected displacements of O atoms might be attributed to the fact that the Ti atom closest to the defect has a *negative effective charge* because it has received extra electrons. This can cause some repulsion between this atom and the four O atoms in the defective region, leading to their outward movements. It also should be pointed out that the same small contribution to the wave function of the F centre comes from these four O atom neighbours of the defect. The relaxation energy obtained for this case is equal to 1.30 eV.

Table 5. Main contributions to the wavefunctions of the F centres.

Type of surface	Phase	Atom	AO type	Coefficient of AO
Sr-O	Cubic	Sr	5s	0.476 19
Sr-O	Tetragonal	Ti	3d <sub>xy</sub>	0.912 00
Ti-O <sub>2</sub>	Cubic	Ti	3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>	0.401 41
		Ti	3d <sub>z<sup>2</sup></sub>	0.343 04

The exploration of the F centre on Ti–O<sub>2</sub> surface for the cubic phase shows smaller atomic displacements in the region of the defect compared with the two previous cases. In particular, the nearest Ti and Sr atoms move outwards from the F centre by 0.05 and 0.07 Å respectively while the distortion of the O atoms closest to the defect is even smaller. The two O atoms from the atomic slab next to the surface move outwards by 0.02 Å and the four O atoms within the surface layer move towards the defect by 0.04 Å. The calculated value of the relaxation energy is equal to 0.31 eV. As follows from table 5, the extra electrons are localized on the two Ti atoms which are nearest to the defect and are situated on the surface. It can be noted that the two O atoms moving outwards from the F centre contribute slightly to the wavefunction of the defect. Thus, similarly to the F centre on the Sr–O surface of the cubic phase, the extra electrons tend to remain on the surface layer. Comparing our results with other studies on F centres, for example in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal (Stashans *et al.* 1994, Kotomin *et al.* 1995) using the same computer code, we can see that wavefunctions of these defects in SrTiO<sub>3</sub> are more extended. Apparently, a considerable degree of covalency of the chemical bonding in SrTiO<sub>3</sub> is the main factor why the F centres are not well localized in this material.

### 3.4. Optical properties

We attempted to calculate absorption energies for the F centres. This was performed using the so-called  $\Delta$ SCF method. Note that the  $\Delta$ SCF energies should be discussed rather than the difference between the relevant one-electron (orbital) energies, which give only rough estimates for the absorption energies in the case of local energy levels. As a result, we found that for the F centre on the Sr–O surface of the tetragonal phase one can anticipate a 3d  $\rightarrow$  4p transition, specifically a 3d<sub>xy</sub>  $\rightarrow$  4p<sub>z</sub> transition, which gives us a value of 2.1 eV for the absorption energy. In the case of the Ti–O<sub>2</sub> surface of the cubic phase we found the possibility of d  $\rightarrow$  d transitions, which gives us a value of 0.6 eV for the absorption energy. Our predicted absorption energy value of 2.1 eV coincides with one of the experimental absorption peaks (Lebedeva 1992) observed in fast-electron (4 MeV) irradiation of SrTiO<sub>3</sub>.

## §4. CONCLUSIONS

We have presented a computational study of O vacancies and F centres on the SrTiO<sub>3</sub>(001) surfaces. The structural, electronic and optical properties are studied within the same computational method and applying the same physical model to describe the surface. The atomic displacements obtained around these defects indicate the significant role of the Coulomb interaction in this semi-ionic material. The wavefunctions of the F centres are found to be more delocalized (extended) than in previous studies (Stashans *et al.* 1994, Kotomin *et al.* 1995) in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal, where the same computational method was utilized. We explain this fact by the importance of the covalency in the chemical bonding of SrTiO<sub>3</sub>, which leads to more extended wavefunctions of the F centres. One of the absorption energies obtained matches the experimentally observed value (Lebedeva 1992) of 2.1 eV found in fast-electron (4 MeV) irradiation of SrTiO<sub>3</sub>.

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