

Radiation defects on SrTiO₃ polar and non-polar surfaces

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ABSTRACT

Using the INDO quantum-chemical computational method we focus on oxygen-vacancy and F centre defects on the non-polar (001) and polar (110) SrTiO₃ surfaces considering both cubic and tetragonal lattices of the material. The results obtained for the lattice relaxation around the defects on the polar (110) surface point to the significant role of the Coulomb interaction in this semi-ionic material. However, in the case of the oxygen vacancies the analysis of the electronic density redistribution leads to the conclusion that these defects make material more covalent due to the stronger hybridisation between the O 2p and Ti 3d states. Wave functions of the F centres are found on the two defect-closest Sr atoms in an agreement with the available scanning microscopy and spectroscopy data and pointing to localisation of two electrons within the O vacancy region. The analysis of the properties of O vacancies and F centres on the non-polar (001) surface points to somewhat different pattern. In particular, the wave functions of the F centres are found on the defect-nearest Ti atoms and are rather extended. One of the absorption energies obtained by the Δ SCF method matches the experimentally observed value of 2.1 eV found in fast-electron irradiation of strontium titanate.

Keywords: SrTiO₃, surfaces, O vacancy, F center, Hartree-Fock method

1. INTRODUCTION

Among the transition-metal oxides, the surface properties of SrTiO₃ have been studied extensively by a number of groups, motivated to a large extent by its numerous applications. The strontium titanate surfaces have become of technological importance due to their catalytic properties¹, their use as epitaxial growth substrates for the high temperature superconductor (HTSC) thin films and in the high T_c -based heterostructures.² It is well recognized that the surface defects such as oxygen vacancies play an important role as reaction centres in the catalytic processes. Therefore, it is necessary and important to study the effect of surface oxygen vacancies on the electronic and structural properties of the SrTiO₃ crystal. In contrast to the (100) surfaces, basic properties of the SrTiO₃ (110) surfaces have not been sufficiently studied up to date though this surface is a popular substrate for epitaxial growth of the so-called a -axis oriented HTSC films. These films compose junction devices in which superconducting tunnelling is expected to take place in parallel to the two-dimensional CuO₂ planes.

In the present work, the electronic and structural properties of the SrTiO₃ (001) and (110) surfaces containing oxygen-vacancy defects are investigated by means of the advanced quantum-chemical method developed for crystals and the so-called large unit cell (LUC) model, which accounts for translational invariance of the crystal.³ We would like to note that the method has already been applied successfully for surface studies of different crystals. Some examples include the study of OH⁻ adsorption on the perfect TiO₂ (001) rutile surface⁴, and calculation of organic adsorbates on the rutile (110) surface.⁵

2. OUTLINE OF THE METHOD AND PURE SURFACE CHARACTERISATION

The employed method of periodically repeated large unit cells (LUCs)³ is designed for the calculation of the total energy and electronic structure of crystals. We preferred to use the LUC model because of its advantage compared to different cluster models, for example, a better treatment of the exchange interaction. A full discussion of the computational relations for calculating the total energy of the crystal within the framework of the LUC approach is given elsewhere.^{3,6}

The method is based on a semi-empirical modification of the molecular orbital (MO) theory with a specific parametrization scheme.⁷ Some atomic parameters are used to reproduce main features of a given crystal and to reduce considerably the

computational time. Thus the method is not cumbersome and is applicable to extended systems with a complex structure and a mixed chemical bonding. The SrTiO₃ crystal has been parameterized by us before⁸ where also details of the bulk crystal properties are given. The numerical values of atomic parameters are shown in Table 1.

As demonstrated by numerous computations,³⁻⁶ 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 and/or surface. Hence we have chosen to exploit 27-fold symmetrically extended LUC consisting of 135 atoms for the SrTiO₃ (001) surface. 16-fold symmetrically extended LUC consisting of 80 atoms was used for the SrTiO₃ (110) surface. In both cases the surface was modelled as a single slab applying two-dimensional periodicity. The bulk lattice parameters, $a = 3.90$ Å for the cubic structure and $a = 3.88$ Å, $c = 3.92$ Å for the tetragonal lattice, fitted by us before^{8,9} were used. It is worth to mention that the current computation method has already been applied to strontium titanate, giving encouraging results. In particular, we have studied impurity doping in the cubic and tetragonal phases of the SrTiO₃ crystal,^{8,10-12} hole polarons^{9,13} and F centres in the crystal bulk.¹⁴

Table 1. Atomic parameters used in the present work (a) and two-centre parameters α_{tB} (au⁻¹) with the numbers in the parenthesis showing the corresponding parameter for the tetragonal phase (b).

(a)					
Atom	AO	ζ (au)	E_{neg} (eV)	P^0 (e)	β (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
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	

Properties of a pure SrTiO₃ non-polar (001) surface are described in detail in Ref. 6. Briefly we can state that due to the surface creation inward movements of atoms situated on the topmost layers were observed. The magnitude of these displacements did not exceed 0.06 Å. The effect of the optical band-gap reduction due to the surface creation was also observed. We calculated the corresponding values of the band-gap width for both phases as a difference between the total energies for the self-consistent-field (SCF) ground and excited states, denoted ΔSCF , 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 ΔSCF method do not coincide with the difference between the relevant one-electron energies, which usually gives only a rough estimation for the optical band-gap width. The optical band-gap magnitudes obtained thereby were found to be equal to 4.2 eV and 4.1 eV for the cubic and tetragonal phase respectively. This is somewhat less than in the case of the bulk SrTiO₃ calculations,^{8,9} where we found values of 4.5 eV and 4.4 eV for the cubic and tetragonal phases, respectively. As can be seen, our band-gap values are somewhat larger than the experimental value of 3.2 eV.¹⁵ Overestimation of the band-gap width originates from neglecting the effect of the long-range electron correlation, which is a common fault of the Hartree-Fock theory. However, one can observe the tendency of band-gap narrowing due to the surface creation.

The SrTiO₃ (110) surface is a polar one. This means that it consists of periodically repeated positively and negatively charged atomic layers. The negatively charged layers contain only oxygens while the positively charged layers consist of O, Ti and Sr atoms. In order to characterise the perfect SrTiO₃ (110) surface, the equilibrium geometry was calculated by us before¹⁶ allowing relaxing all atoms in the two surface-topmost layers from both sides of the slab. As a result it was found that atomic movements within the plains parallel to the surface are negligible while their relaxation in the direction

perpendicular to the surface is considerable. A full description of atomic displacements is given in detail in Ref. 16. Briefly we can state that the atomic relaxation can be understood taking into account the polar character of the surface and consequently the importance of the Coulomb electrostatic interaction. Here we refer to some opposite movements of atoms situated on the slab's border. Since different layers have opposite electrical charge they experience opposite displacements due to the Coulomb law. In general, the magnitude of atomic movements is about 0.2-0.3 Å. In our mind, the obtained larger atomic displacements compared to the pure SrTiO₃ (001) surface are due to the fact that the SrTiO₃ (110) surface is a polar one. These results also support the idea that the observed drastic modification of the surface cannot be related only to the formation of point defects but have to be interpreted in terms of the formation of the so-called non-perovskite phases.¹⁷ The atomic relaxation was performed for both cubic and tetragonal structures of the SrTiO₃ crystal. We did not find, however, noticeable differences in the surface reconstruction for these two crystallographic structures. A bit smaller, around 0.02 Å, atomic movements for the tetragonal lattice were observed. The calculated relaxation energy as a difference between the total energies for the fully relaxed and unrelaxed systems, were found to be equal to 10.3 and 9.3 eV for the cubic and tetragonal lattices, respectively. Similar to the previous case of the SrTiO₃ (001) surface we have observed a small reduction of the band-gap width due to the surface creation. We have also obtained less negative charges on oxygens and less positive charges on titaniums for the tetragonal structure. This effect points to the fact that the tetragonal lattice has higher degree of covalency due to the stronger hybridisation between the O 2p and Ti 3d states.

3. OXYGEN-VACANCY DEFECTS ON SrTiO₃ (001) SURFACE

In order to investigate oxygen vacancies on the SrTiO₃ (001) surfaces and their influence upon different material properties we made use of 135-atom LUC taking out one oxygen ion, that is creating a vacancy, V_O. SrTiO₃ consists of successive Ti-O₂ and Sr-O plains; so two kinds of (001) surface are possible: (i) Sr-O surface, and (ii) Ti-O₂ surface. That is why we studied V_O on these two different surfaces and also considered two different crystallographic phases: cubic and tetragonal.

In the case of V_O situated on the Sr-O surface, V_O 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 the distance of 2.67 Å belonging to the layer composed of Ti and O atoms next to the surface. As a result of automated geometry optimization we have found that the atoms relax according to the Coulomb electrostatic interaction law. The positively charged Ti and Sr atoms move outwards the positively charged V_O by 0.03 and 0.07 Å, respectively. These displacements are symmetrical, i.e. 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_O 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.

In the case of the tetragonal SrTiO₃ structure we observe similar lattice distortion due to the presence of V_O 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. The relaxation energy obtained for this case is equal to 1.40 eV.

In the case of V_O on the Ti-O₂ surface of the cubic SrTiO₃ structure the V_O has two Ti atoms at a distance 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 <100> and <101> directions for the Ti and Sr atoms, respectively. The O atoms move towards the positively charged defect. 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 V_O on the Ti-O₂ surface of the tetragonal phase but did not achieve the convergence required. It is possible therefore that the surface turns to be unstable due to the V_O presence or that considerable rearrangement or reconstruction is necessary to stabilise it. This is also in accordance with the experimental ultrahigh-vacuum annealing studies¹⁸ of the SrTiO₃ (001) surfaces where it was found that the Sr-O bonding on the topmost Sr-O plane is more stable than Ti-O bonding on the Ti-O₂ topmost layer.

As it follows from ultraviolet photoelectron spectroscopy observations¹⁹ a shallow level appears in the band-gap due to surface O-vacancy defects on the SrTiO₃ (001) reduced surface. This might be attributed to the presence of F centre. Similarly as for the V_O, we computed this point defect for three cases: (i) the F centre on the Sr-O surface of the cubic

structure; (ii) the F centre on Ti-O₂ surface of the cubic structure; and finally, (iii) the F centre on the Sr-O surface of the tetragonal structure.

Studies of the F centre on the Sr-O surface of the cubic SrTiO₃ show the following pattern of the atomic displacements. The Ti atom closest to the defect and the four defect-surrounding Sr atoms 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_O 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 localised on the four nearest Sr atoms 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 the defect by 0.05 and 0.15 Å, respectively, there are also outward movements of the four defect-nearest O atoms by 0.08 Å. The wave function 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 defect-closest Ti atom has a *negative effective charge* because it has received extra electrons. This can cause some repulsion between this atom and the four oxygens in the defective region, leading to their outward movements. It also should be pointed out that small contribution to the wave function of the F centre comes from these four defect-neighbouring O atoms. The relaxation energy obtained for this case is equal to 1.30 eV.

The exploration of the F centre on Ti-O₂ surface for the cubic phase shows smaller atomic displacements in the defective region 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 defect-closest O atoms 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. The extra electrons are localized on the two defect-neighbouring Ti atoms situated on the surface. It can be noted that the two oxygens moving outwards from the F centre contribute slightly to the wave function 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. Generally speaking we can notice that wave functions of the F centres in SrTiO₃ are rather extended. Apparently, a considerable degree of covalency of the chemical bonding in SrTiO₃ is the main factor why the F centres are not well localised in this material.

We attempted to calculate absorption energies for the F centres. This was done using the Δ SCF method. 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_{xy} \Rightarrow 4p_z transition, which gives us a value of 2.1 eV for the absorption energy. In the case of the Ti-O₂ 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 peaks²⁰ observed in fast-electron (4 MeV) irradiation of SrTiO₃.

4. OXYGEN-VACANCY DEFECTS ON SrTiO₃ (110) SURFACE

In order to study oxygen vacancies on the SrTiO₃ (110) surface and their influence upon different material properties, we made use of 80-atom LUC taking out one oxygen ion, i.e., creating a vacancy, V_O. As it is shown in Fig. 1, the V_O finds itself surrounded by all three types of atoms. In order to obtain the energy-minimum configuration, we allowed nineteen defect-closest atoms to move freely from their initial lattice sites. The automated geometry optimization procedure was exploited to reach the equilibrium configuration of the system (see Fig. 1). As a result the atomic movements were found not to exceed 0.06 and 0.05 Å for the cubic and tetragonal phases, respectively. Thus the magnitude of the atomic movements is of the same order as for the V_O studies on the SrTiO₃ (001) non-polar surface. The atomic relaxation, in general, obeys the Coulomb electrostatic interaction law. The positively charged Ti and Sr atoms move outwards from the positively charged V_O, while the negatively charged O atoms move towards the V_O. The calculated relaxation energy, E_{rel}, as a difference between the relaxed and unrelaxed crystal states containing V_O was found to be equal to 9.67 and 7.62 eV for the cubic and tetragonal phases, respectively. Although the magnitude of relaxation is not very large we obtain considerable values for the relaxation energies. This might be explained by noticeable electronic density redistribution in the defective region due to the V_O presence. The fact that the E_{rel} is larger for the cubic phase might be explained by slightly larger atomic displacements in this phase and also due to the more rigid crystalline lattice in the tetragonal phase existing at lower temperatures.

Our study shows that there exists electronic density redistribution due to the V_O creation. A short analysis points to the following general tendency in the charge redistribution. The V_O-surrounding negative O atoms become a bit less negative

and the defect-closest Ti atoms become a bit less positive. This implies that the V_0 changes slightly the nature of the chemical bonding between the atoms situated in the defective region making it more covalent especially between the Ti and O atoms.

Two electrons were added to the system containing V_0 to study F centres and their influence upon the structural and electronic properties of the material. Similarly as for the V_0 , we computed this point defect for both crystallographic lattices of the SrTiO_3 crystal. The summarised results of atomic displacements around the F centre are shown in Fig. 1. The directions of atomic movements, in general, remain the same as for the V_0 but their magnitudes diminish. This is anticipated because instead of the positively charged V_0 point defect we have “neutral” F centre. The obtained relaxation energies are also considerably smaller compared to the case of the V_0 defects. The obtained values of E_{rel} are equal to 4.26 and 2.50 eV for the cubic and tetragonal structures, respectively.

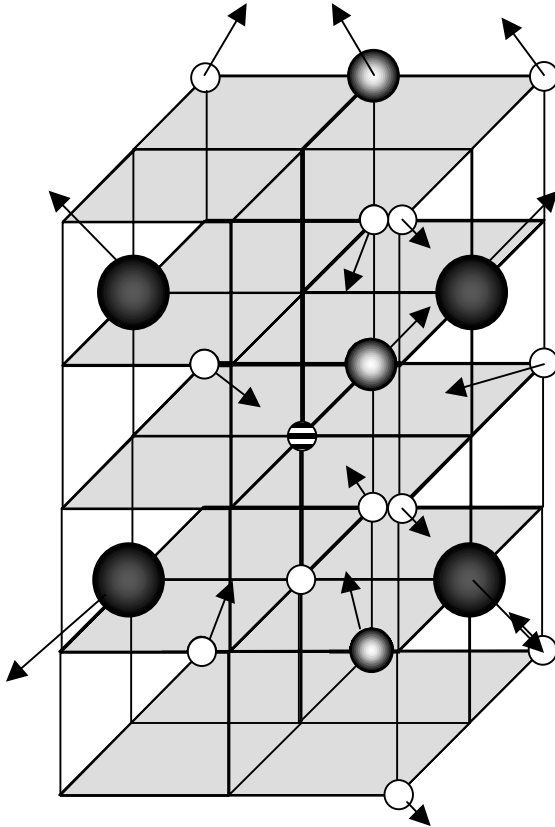


Fig. 1. V_0 or F centre, shown dashed, on the SrTiO_3 (110) surface and its surrounding along the vertical $\langle 001 \rangle$ direction. Small, medium and large spheres denote O, Ti and Sr atoms, respectively. The arrows show the directions of atomic movements.

Analysis of charges on atoms situated around the F centre shows considerable electronic density redistribution for the two Sr atoms situated along the $\langle 101 \rangle$ and $\langle 10\bar{1} \rangle$ directions with respect to the F centre and being the two defect-closest atoms. This implies that the F centre is well localised within the O vacancy region. The result of the electron density redistribution on the defect-closest Sr atoms is somewhat different from the studies for the SrTiO_3 (001) surface described above, where the wave function of the two extra electrons was found on the defect-closest Ti atoms.

The important feature of any material is the occurrence of electronic states within the band-gap region due to the F centres. As it was established before for the SrTiO_3 (100) surface, the in-gap electronic states are ascribed to the Ti 3d – O vacancy complexes.^{21,22} This was also confirmed in our previous calculations⁶ for this type of surface. However, in the case of the SrTiO_3 (110) surface, we find an electronic state in the middle of the energy gap composed mainly of the Sr states of the two defect-closest Sr atoms. This is true for both, cubic and tetragonal structures. In our mind, this occurs due to the different surface morphology and the fact that for the (110) surface Ti atoms turn to be considerably less positive compared

to the (001) surface case. This unexpected result is in an agreement with the scanning microscopy and spectroscopy data²³ as well as the theoretical analysis of charge transfer phenomenon²⁴ in the SrTiO₃ crystal.

5. CONCLUSIONS

We have presented the computational study of oxygen vacancies and F centres on the SrTiO₃ (001) and (110) 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 crystal. However, in the case of the oxygen vacancies the analysis of the electronic density redistribution leads to the conclusion that these defects make material more covalent due to the stronger hybridisation between the O 2p and Ti 3d states. This effect is especially obvious for the defects on the polar (110) surface.

The wave functions of the F centres are found to be more delocalized (extended) than in previous studies in the α -Al₂O₃ crystal^{25,26} and on the MgO (100) surface.²⁷ We explain this fact by considerably larger covalency in the chemical bonding of SrTiO₃ compared to that in the α -Al₂O₃ and MgO crystals. The larger covalency leads to more extended wave functions of the F centres. One of the absorption energies obtained for the F centre on the (001) surface matches the experimentally observed value of 2.1 eV²⁰ found in fast-electron (4 MeV) irradiation of SrTiO₃.

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