



## Computational study of structural and electronic properties of superconducting La-doped SrTiO<sub>3</sub>

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### ABSTRACT

Motivated by discovery of the superconductivity in strontium titanate (SrTiO<sub>3</sub>) doped with a small number of electron carriers, we have carried out quantum-chemical Hartree–Fock calculations to study La-doped SrTiO<sub>3</sub>. The crystalline lattice distortion due to the impurity presence is obtained for both cubic and tetragonal structures. The atomic movements in a region surrounding the defects show considerable differences for two crystallographic phases. La-induced local energy levels are found in the gap between the upper valence band and the conduction band. Two different states of the system, namely singlet and triplet states, are considered. These states occur depending on how the extra electrons fill in the local energy levels. The observed electron transfer from the local energy levels to the conduction band is discussed in the light of the available experimental data on the superconductivity studies.

### §1. INTRODUCTION

The perovskites are an extremely important class of ceramic materials. These compounds have a chemical formula ABO<sub>3</sub> where A is either a monovalent or divalent cation and B is either a pentavalent or tetravalent metal. Strontium titanate (SrTiO<sub>3</sub>) is possibly the best-known example of the cubic perovskite crystals with the space group *Pm3m*, where Ti atoms are at the cube centres, Sr atoms at the cube corners and O atoms at the edge centres. The primitive unit cell of the crystal contains one formula unit of SrTiO<sub>3</sub>, that is five atoms. Strontium titanate is one of the most widely used electronic ceramic materials, which has a perovskite-type structure. Typical applications are used as a grain-boundary barrier layer capacitor (Fujimoto and Kingery 1985), oxygen-gas sensor (Gerblinger and Meixner 1991), epitaxial growth substrate for high-temperature superconductor thin films (Kawai *et al.* 1991) and catalytic material (Mavroides *et al.* 1976). SrTiO<sub>3</sub> has also been known to become superconducting when a small number of electron carriers are doped by La substitution for a Sr atom (Aiura *et al.* 1996).

Trying to explain some effects in the superconducting (Aiura *et al.* 1996, Suzuki *et al.* 1996) La-doped SrTiO<sub>3</sub> below 14 K is our main reason to study this specific kind of doping. From the experiments carried out in Japan (Aiura *et al.* 1996, Suzuki *et al.* 1996), two peaks in the bandgap region are induced by substitution of La for Sr: a metallic peak and a peak at about 1.5 eV within the bandgap. These

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measurements also indicated that the spectral intensities of both peaks increase with increasing La concentration, and superconductivity occurs below 14 K when the impurity concentration corresponds to  $\text{La}_{0.05}\text{Sr}_{0.95}\text{TiO}_3$ . It has to be noted that none of these facts has a satisfactory fundamental explanation. From our studies, the two different levels within the bandgap region may be attributed to the presence of two different states of the system. In addition, we believe that a La impurity within the crystal may act as a centre for a new phase (Cowley 1996). Therefore, we have tried to find the best possible positions of the atoms around the impurity atom, applying also an automated geometry optimization procedure. It seems that the phenomenon of ferroelectricity in the  $\text{SrTiO}_3$  crystal plays an important role in the way that the host atoms reach their new equilibrium positions.

In order to make our calculations we have used the intermediate neglect of differential overlap (INDO) method modified for crystals and a specific parametrization scheme (Shluger 1985) as implemented into the CLUSTERD computer code. We have modelled the La doping in the cubic and tetragonal crystalline lattices of  $\text{SrTiO}_3$  using the periodic large-unit-cell (LUC) model (Shluger and Stefanovich 1990). Up to now this method has been successfully employed to investigate a number of perfect and defective oxides (Shluger and Itoh 1990, Jacobs and Kotomin 1992, Jacobs *et al.* 1992, Stashans *et al.* 1994, Kotomin *et al.* 1995) and materials with a simpler electronic band structure. This technique is based on the molecular orbital (MO) theory (Pople and Beveridge 1970). The LUC model calculates both the electronic structure and the total energy of the crystal via MOs as a linear combination of atomic orbitals (AOs).

The objective of this work is to study the influence of La impurity upon the electronic and structural properties of  $\text{SrTiO}_3$ . The work has been carried out in such a way as to analyse the properties of the cubic (paraelectric) phase versus the tetragonal (ferroelectric) phase, which becomes superconducting below 14 K.

## §2. OUTLINE OF THE COMPUTATIONAL METHOD

As mentioned above, the computational technique is based on the MO theory and the LUC model. The Fock matrix elements in the INDO approximation modified for crystals (Shluger 1985, Stefanovich *et al.* 1990) contain the following semi-empirical or numerical parameters:  $\zeta$ ,  $E_{\text{neg}}$ ,  $P^{(0)}$ ,  $\alpha$  and  $\beta$ . The parametrization scheme is of a primary importance. The INDO parameter set for a particular element is optimized to match the main experimental features of the studied crystal, such as the electronic band structure, the effective charges on the atoms and the lattice parameters. In addition, this method may be used to calculate and match basic properties of some selected test molecules, for example the equilibrium distance between the atoms in the molecule and the ionization potentials. The parameter sets utilized in the present work were taken from Stefanovich *et al.* (1990) for the O 2s and 2p AOs, from Pinto and Stashans (2000) for the Ti 3d, 4s and 4p AOs and from Stashans and Sánchez (2000) for the Sr 4p and 5s AOs as well as the La 5d, 6s, 6p 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. It should be noted that, in particular, the method reproduced very well the electron affinity of  $\text{La}^+$  (first ionization potential). Our obtained value of 5.64 eV is very close to the experimental magnitude (Weast 1979) of 5.61 eV.

Table 1. Semiempirical parameter sets used in the present work.

Atom	AO	$\zeta$	$E_{\text{neg}}$	$P^0$	$\beta$
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

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

A	$\alpha_{\mu\text{B}}(\text{au}^{-1})$			
	B $\equiv$ Sr	B $\equiv$ Ti	B $\equiv$ O	B $\equiv$ 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

There are two models implemented in the computer code:

- (i) the periodic LUC (Shluger and Stefanovich 1990, Smith *et al.* 1985) and
- (ii) the embedded molecular cluster (EMC) model (Kantorovich 1988), which is also based on a strict treatment of the total energy of the whole crystal, accounting for the perturbation (polarization) that the remaining crystal has on the EMC region, thus leading to the so-called quantum cluster approach.

In this investigation the LUC model has been used mainly because it has been proved to be very reliable in a number of different applications (Shluger and Stefanovich 1990, Stashans *et al.* 1996, Lunell *et al.* 1997). It has to be noted that the periodic LUC model considers the electronic band structure and calculates the total energy of the system more accurately than the EMC not only because of the periodicity condition but also owing to a more careful treatment of exchange interaction, which is omitted in the EMC case between the EMC region and the rest of the crystal. In this model the Coulomb interaction is treated quite well because of the theory of special  $\mathbf{k}$  points (Evarestov 1982). The Coulomb lattice sums are calculated using the Ewald (Born and Huang 1954) method, which was generalized to the case of an arbitrary lattice. Finally, the exchange interaction is computed after introducing the so-called cut-off function (Shidlovskaya *et al.* 1988). We would like to note that the current computational scheme has already been used successfully in studies of a number of perovskite-type crystals. In particular, the phase transition (Eglitis *et al.* 1996), the atomic and electronic structures of F centres (Kotomin *et al.* 1998) and bound-hole polarons (Kotomin *et al.* 1999) were studied in a KNbO<sub>3</sub> crystal, giving

very encouraging results. Recently, our computer code was used to investigate different acceptor impurities and hole self-trapping in the  $\text{BaTiO}_3$  crystal (Pinto and Stashans 2000, Pinto *et al.* 2000, Stashans and Pinto 2000), the donor-doping effect upon structural and electronic properties in the  $\text{CaTiO}_3$  crystal (Erazo and Stashans 2000) and calculation of different point defects in the  $\text{SrTiO}_3$  crystal (Stashans and Sánchez 2000, Stashans 2001). It should be noted that a first attempt to study La doping in the cubic and tetragonal crystalline lattices of the  $\text{SrTiO}_3$  crystal has already been made (Stashans and Sánchez 2000).

### § 3. RESULTS AND DISCUSSION

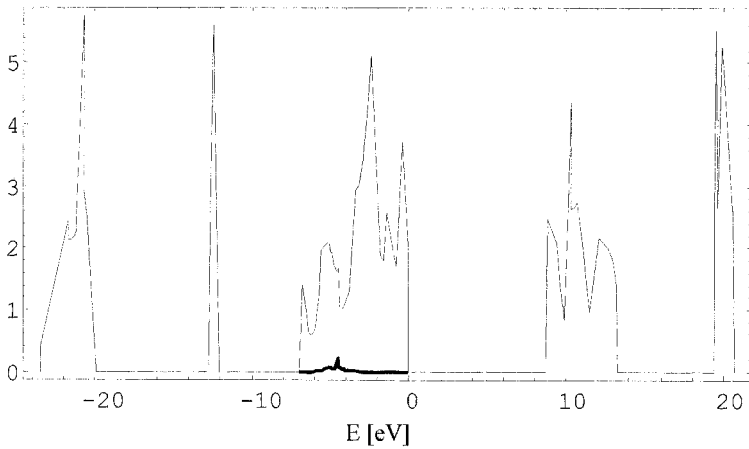
Our calculations have been performed to study the La-impurity effects in both known crystallographic phases, cubic and tetragonal, of the  $\text{SrTiO}_3$  crystal. Three different LUC sizes have been exploited, that is we carried out our computations in LUCs of 40, 80 and 160 atoms respectively. In the cases of 80- and 160-atom LUCs we have substituted two La atoms for Sr atoms. This was done to explain the origin of two different energy peaks observed experimentally (Aiura *et al.* 1996, Suzuki *et al.* 1996) within the bandgap of the material.

#### 3.1. *A short report on the structural and electronic properties of pure $\text{SrTiO}_3$*

Our computational approach has already been applied to study pure  $\text{SrTiO}_3$  cubic phase (Stashans 2001), giving satisfactory results. In general, we managed to reproduce successfully the spatial characteristics of both crystalline lattices. The obtained lattice constants were found to be equal to  $a = 3.90 \text{ \AA}$  for the cubic lattice, and  $a = 3.88 \text{ \AA}$  and  $c = 3.92 \text{ \AA}$  for the tetragonal lattice. All these values almost coincide with the corresponding experimental values (Wyckoff 1960). In the tetragonal phase, the positions of O atoms (tilted O octahedra) were optimized by the method, giving O displacements in the course of tilting equal to  $0.06 \text{ \AA}$ . Despite its semiempirical character the computational code used in the present work is very precise in reproducing crystal structures and phase transitions, including small energy differences related to the ferroelectric instability (Eglitis *et al.* 1996) as was demonstrated for  $\text{KNbO}_3$ . Although our task was not concerned with study of the phase transition in this material, we managed to reproduce the fact that the tetragonal structure is more stable than the cubic structure by  $0.03 \text{ eV}$ .

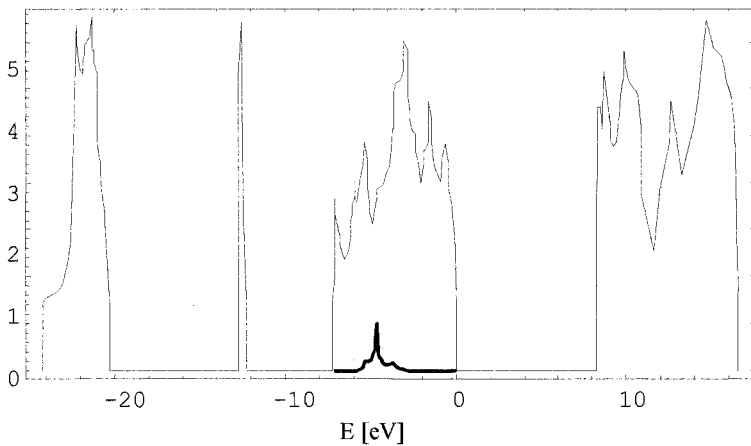
The densities of states (DOSs) for both crystalline lattices are shown in figure 1. The widths and compositions of the valence bands are in a very good agreement with the X-ray photoelectron spectra measurements (Pertosa and Michel-Calendini 1978). The lower valence band (LVB) is mainly composed of O 2s states while the UVB is predominantly O 2p in nature. A considerable admixture of Ti 3d states was found in the UVB for the tetragonal phase (figure 1(b)), which testifies to the importance of the covalent bonding and Ti 3d–O 2p hybridization. In addition, from figure 1, the subband of Sr 4p states lies between the UVB and LVB. This energy band is very narrow, having a width of only  $0.2 \text{ eV}$ . We considered it essential to include the Sr 4p states as the basis AOs within the valence basis set since their overlapping with AOs of the other atoms is not negligible. With respect to the conduction band (CB) we have to point out to the Ti 3d states forming the bottom of this band. The values of the bandgap width for both phases were computed as the difference  $\Delta\text{SCF}$  between the total energies of the self-consistent-field (SCF) ground and excited states, which corresponds to electron excitation from the highest occupied MO to the lowest energy level in the CB. Thus energies obtained by the  $\Delta\text{SCF}$  method do not coincide

Arbitrary Units



(a)

Arbitrary Units



(b)

Figure 1. DOSs for (a) the cubic and (b) the tetragonal structures of pure SrTiO<sub>3</sub> crystal. The bold curve in the upper valence band (UVB) denoting Ti 3d states indicates the considerable covalence effects in the tetragonal phase. The 'zero' value of the energy is attributed to the UVB.

with the difference between the corresponding one-electron energies, which usually gives only a rough estimation of the optical bandgap width. The bandgap width magnitudes obtained thereby were found to be equal to 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.

Finally, we would like to note that the LUC of 40 atoms, eight times ( $2 \times 2 \times 2$ ) the extended primitive unit cell, was used to reproduce the main structural and electronic properties of the pure substance for both phases.

### 3.2. Large unit cell of 40 atoms

In order to study impurity doping, the La atom was inserted instead of one of the Sr atoms in the central region of the LUC. The arrangement of atoms for the LUC of 40 atoms in the cubic phase is represented in figure 2. The rhombus represents the impurity La atom. It should be noted that we are replacing a Sr atom by a La atom, which has one extra electron in its electronic configuration in comparison with the Sr configuration. This insertion causes a crystal lattice perturbation, which leads to variation in the original positions of the atoms around the impurity. The same atomic arrangement was used for the tetragonal phase.

The most external Sr and Ti atoms are situated very far from the inserted La atom and as a result do not suffer any relaxation as will be shown later. Consequently, the notation scheme used to describe atomic displacements is shown in figure 3. The numbers coincide with those given in the tables for both cubic and tetragonal phases.

Our calculations show that in the cubic phase the atomic displacements around the La atom are completely symmetric. The eight Ti atoms nearest to La move outwards by about  $0.07 \text{ \AA}$  along the  $\langle 111 \rangle$  directions while the twelve O atoms closest to La move towards the La impurity by about  $0.03 \text{ \AA}$  along the  $\langle 110 \rangle$  directions. On the other hand, for the tetragonal phase the displacements are symmetric along the  $x$  and  $y$  axes while there is obvious asymmetry in the  $z$  axis.

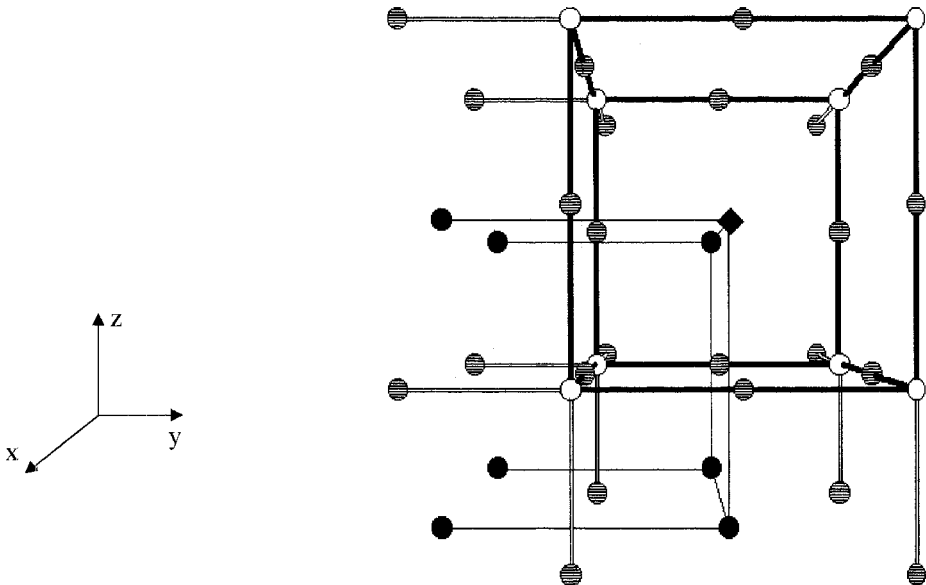


Figure 2. Atomic arrangement in the LUC consisting of 40 atoms used in the present calculations: (○), Ti atoms; (●), Sr atoms; (◐), O atoms; (◆) La impurity, which is inserted instead of one of the Sr atoms.

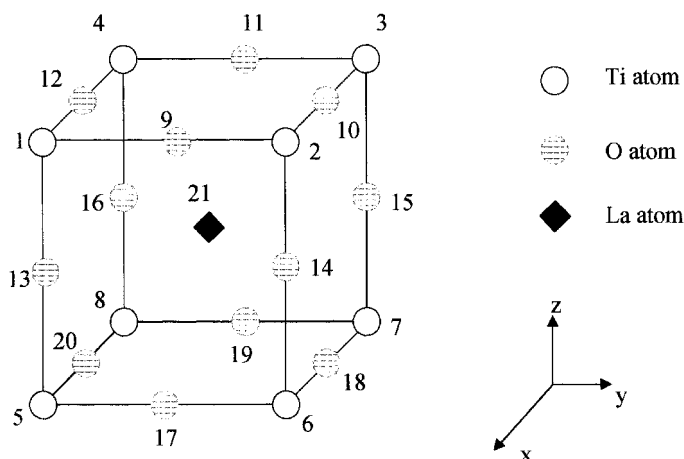


Figure 3. A general schematic diagram shows the vicinity of the inserted La atom.

The important result that we have found is that the inclusion of the La atom produces the occurrence of a one-electron local energy level within the gap between the UVB and the CB. This local energy level is situated around 2.05 and 1.98 eV above the top of the UVB in the cubic and tetragonal phases respectively.

### 3.3. Large unit cell of 80 atoms

In order to form a LUC of 80 atoms we have extended twice the LUC of 40 atoms along the  $x$  axis, that is two LUCs of 40 atoms have been placed together. Because all directions in the cubic phase are equivalent, choosing any other direction would have the same result.

In the system of 80 atoms (cubic and tetragonal phases) we have replaced two La atoms by two Sr atoms (figure 4) and have obtained two different states of the system, namely a singlet state and a triplet state. The singlet state corresponds to the case when two extra electrons occupy the same local energy level within the band-gap and the triplet state occurs when two electrons occupy two different local energy levels. This was done to analyse and explain some experimental results of the photo-emission spectroscopy measurements (Aiura *et al.* 1996).

We have found that the amounts of relaxation for each state and phase are different. Also, there are differences in lattice distortion around each of the two La atoms. This effect can be understood as due to the extra electron jump from one of the La atoms to another. The results obtained for the cubic phase are as follows. In the singlet state, the Ti atoms around the second La atom (La(2)), which loses its extra electron, have larger displacements than the atomic movements around the first La atom (La(1)), which receives one electron from La(2). On the other hand, in the triplet state the difference between the atomic displacements around La(1) and La(2) is almost negligible. Here we do not observe the extra electron jump from La(2) to La(1). The detailed atomic displacements for the cubic phase are given in table 3. As can be seen, the general tendency of atomic movements is the same as in the LUC of 40 atoms, that is the O atoms move towards the impurity and the Ti atoms move away from the impurity owing to the Coulomb electrostatic interaction. However, the displacements are not completely radial, as

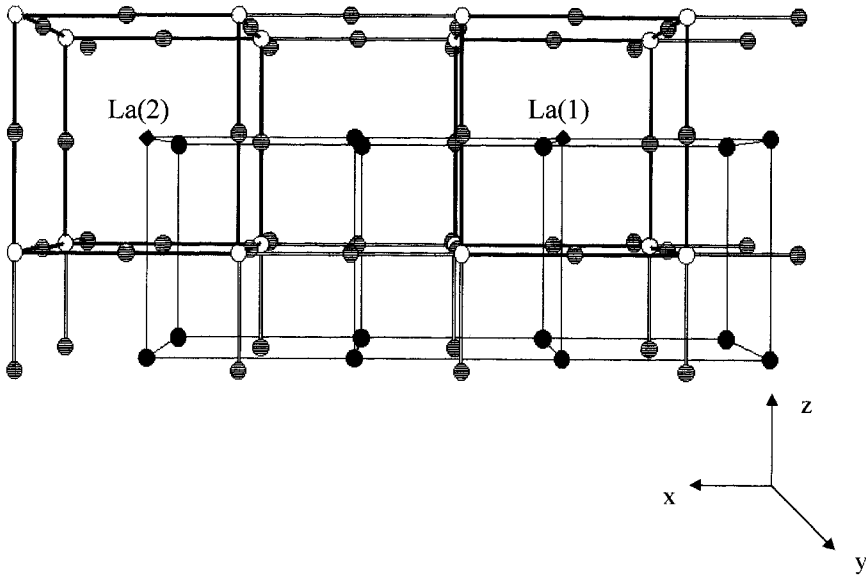


Figure 4. Location of La(1) and La(2) atoms within the LUC of 80 atoms for the cubic phase of the  $\text{SrTiO}_3$  crystal.

Table 3. Atomic displacements in the cubic and tetragonal phases of an 80-atom LUC around La(1) and La(2) atoms. In the cubic phase the extra electron of La(2) transfers to La(1), changing the charge state of both impurity atoms (conversely for the tetragonal phase). The + and - signs denote outward and inward movements respectively with respect to the impurity atom. The atomic numbers correspond to those given in figure 3. The numbers in parentheses are for the case when a given O atom has zero movement along one of the three axes. Additionally, if more than one number is given in parentheses, the first and last numbers indicate the motion for atoms 9, 10, 11 and 12 and for atoms 13, 14, 15 and 16, respectively.

Phase	Atom	Singlet			Triplet		
		$\overset{x}{\underset{\circ}{\text{Å}}}$	$\overset{y}{\underset{\circ}{\text{Å}}}$	$\overset{z}{\underset{\circ}{\text{Å}}}$	$\overset{x}{\underset{\circ}{\text{Å}}}$	$\overset{y}{\underset{\circ}{\text{Å}}}$	$\overset{z}{\underset{\circ}{\text{Å}}}$
Cubic	Ti-La(1)	0.01	0.03	0.04	0.04	0.04	0.04
Cubic	Ti-La(2)	0.06	0.05	0.05	0.03	0.04	0.04
Cubic	O-La(1)	(-0.03)	(-0.03)	(-0.06)	(-0.02)	(-0.02)	(-0.02)
Cubic	O-La(2)	(-0.01)	0	0	(-0.02)	(-0.02)	(-0.02)
Tetragonal	Ti-La(1)	0.05	0.06	0.05	0.04	0.04	0.04
Tetragonal	Ti-La(2)	0.04	0.01	0.03	0.04	0.04	0.04
Tetragonal	O-La(1)	(0.01)	(0.01)	(0.02    -0.02)	(-0.01)	(-0.01)	(-0.01    -0.05)
Tetragonal	O-La(2)	(-0.05)	(-0.01)	(-0.01    -0.05)	(-0.01)	(-0.01)	(0.01    -0.03)

would be expected. In the singlet state, one electron of La(2) jumps to La(1); this changes both impurity charges and affects the structure and its distortion. In contrast, in the triplet state there is no electron transfer and the lattice distortion result is almost the same as for the LUC of 40 atoms.

The atomic displacements in the tetragonal phase show a different pattern from that in the cubic phase. In the singlet state it was found that the relaxation of the



atoms along the  $x$  and  $y$  directions are not the same (see table 3 for more details). One would expect the same atomic movements along these two axes since they are crystallographically equivalent. However, we observe that each of these directions becomes independent and thus we have a reduction in the symmetry of the system. It seems that the atoms around La(1) try to move outwards including some O atoms, while the atoms around La(2) have the same tendency of displacements as in the cubic phase. There are some differences in the lattice distortion for the triplet state of the tetragonal phase as shown in table 3.

For the tetragonal phase, in the singlet state similar to that for the cubic phase we observe one electron transfer from La(2) to La(1), but in the triplet state we observe a new effect; both extra electrons transfer from the local energy levels within the bandgap to the CB. These electrons occupy Ti 3d AOs in the CB. This phenomenon testifies to the occurrence of free electrons in the material, which can contribute to the electrical conductivity and superconductivity below 14 K. This new effect together with the change in the spontaneous electric dipole, which is present in this phase, might lead to the observed unusual atomic displacements along the  $z$  axis.

#### 3.4. Large unit cell of 160 atoms

In order to form a LUC of 160 atoms we have extended the LUC of 40 atoms four times, thus obtaining 32-times ( $4 \times 2 \times 4$ ) or ( $4 \times 4 \times 2$ ) symmetric extensions. We have conserved the positions of the impurities within the LUC; that is in the cubic phase the La atoms are along the  $\langle 100 \rangle$  direction, and in the tetragonal phase along the  $\langle 110 \rangle$ ,  $\langle 010 \rangle$ ,  $\langle 011 \rangle$ ,  $\langle 001 \rangle$  and  $\langle 101 \rangle$  directions (figure 5). We have con-

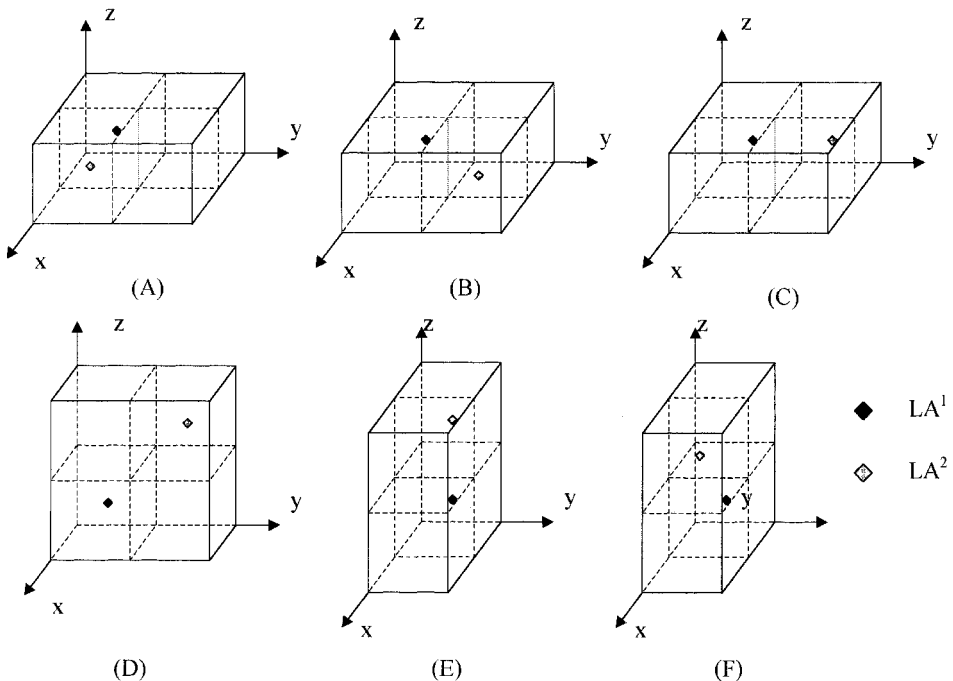


Figure 5. Relative positions of the two La atoms (( $\blacklozenge$ ), La(1); ( $\diamond$ ), La(2)) in the LUC of 160 atoms (a) in the cubic phase and (b)–(f) in the tetragonal phase.

sidered various cases of defect positions in the tetragonal phase in order to understand the importance of the impurity situation with respect to the structural and especially electronic properties of the material. As in the case of 80-atom LUCs we have considered the substitution of two Sr atoms by two La atoms. This means that the system can be in two different states: singlet and triplet. Two impurity atoms in the LUC of 160 atoms give us an impurity concentration equal to  $x = 0.0625$  in the formula  $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ , which is very close to that used in the experimental studies (Aiura *et al.* 1996) ( $x = 0.05$ ).

Our studies of the cubic phase reveal that the inclusion of La causes a reduction in the symmetry of the system. As can be seen from table 4, there are differences in the atomic displacements, at least along one direction. Our studies also show that the singlet state is energetically more favourable than the triplet state and, in the singlet state, one electron is transferred from La(2) to La(1) whereas, in the triplet state, both La atoms keep their electrons.

In the tetragonal phase we observe that the most favourable energy configuration for the singlet state is obtained when the La atoms are situated along the  $\langle 011 \rangle$  direction. On the other hand, the most favourable energy configuration for the triplet state is found when the impurity atoms are situated along the  $\langle 001 \rangle$  direction. This effect might be explained by the fact that certain asymmetry exists in the lattice distortion along the  $y$  axis (see table 4) as mentioned above, that is the impurity acts again as a centre of a new phase. Also, our calculations show that

- (i) the triplet state is more favourable than the singlet state,
- (ii) one electron is transferred from La(1) to La(2) in the singlet state and
- (iii) in the triplet state both La atoms either keep their electrons or lose them depending on their relative positions (in the latter case the extra electrons transfer to the Ti 3d AOs in the CB).

Table 4. Atomic displacements in the cubic and tetragonal phases of a 160-atom LUC around La(1) and La(2) atoms. In the cubic phase the extra electron of La(2) transfers to La(1), changing the charge state of both impurity atoms (conversely for the tetragonal phase). The + and - signs denote the outward and inward movements respectively with respect to the impurity atom. The atomic numbers correspond to those given in figure 3. The numbers in parentheses are for the case when a given O atom has zero movement along one of the three axes. Additionally, if more than one number is given in parentheses, the first, middle and last numbers indicate the motion for atoms 9, 10, 11 and 12, for atoms 13, 14, 15 and 16, and for atoms 17, 18, 19 and 20 respectively.

Phase	Atom	Singlet			Triplet		
		$x$ (Å)	$y$ (Å)	$z$ (Å)	$x$ (Å)	$y$ (Å)	$z$ (Å)
Cubic	Ti-La(1)	0.01	0.03	0.04	0.04	0.04	0.04
Cubic	Ti-La(2)	0.06	0.05	0.05	0.04	0.04	0.04
Cubic	O-La(1)	(-0.03)	(-0.03)	(-0.6)	(-0.2)	(-0.02)	(-0.02)
Cubic	O-La(2)	(-0.01)	(0.02)	0	(-0.02)	(-0.02)	(-0.02)
Tetragonal	Ti-La(1)	0.05	0.06	0.05	0.04	0.04	0.04
Tetragonal	Ti-La(2)	0.04	0.01	0.03	0.04	0.04	0.04
Tetragonal	O-La(1)	(0.01)	(0.01)	(0.02  0)	(-0.01)	(-0.01)	(-0.01   - 0.05)
Tetragonal	O-La(2)	(-0.05)	(-0.01)	(-0.01   - 0.05)	(0.01   - 0.01  0.01)	(-0.01)	(0.01   - 0.03)

Our results indicate that the symmetry of the system is broken (reduced) in both phases. This might happen because the La atoms become the centres of a new phase, or we are dealing with the Jahn–Teller effect (Englman 1972). As can be seen from figures 6 and 7 some atoms having the same atomic charge move in different manners with respect to the same impurity. In the Jahn–Teller theory (Englman 1972) this is the so-called  $e \times E$  problem, and the atomic relaxations will promote the system's total energy reduction by asymmetric movements. We also find that the Ti atoms receiving electrons belong to the Ti–O planes situated perpendicular to the  $z$  axis. Therefore, one can expect superconductivity in this material just in the Ti–O planes. This is in good accordance with the results obtained for cuprates, where the same behaviour is observed for the Cu–O planes (Myers 1997).

In the cases of 80- and 160-atom LUCs we observe two different local energy levels within the bandgap for both states of both systems. This outcome is in accordance with the experimental results (Aiura *et al.* 1996) stating the presence of two local energy levels due to the La doping. It can also be noted that in all cases the composition of the local energy levels in the bandgap is due to the La 6s AO.

When the total energies of the systems with different states are compared, we have found that in the tetragonal phase the triplet state is energetically more favourable than the singlet state. If we use the same comparison for the LUCs of 80 atoms, that is increasing the La concentration twice, the favourability of the triplet state increases even more. This explains the experimental observation of the increase in

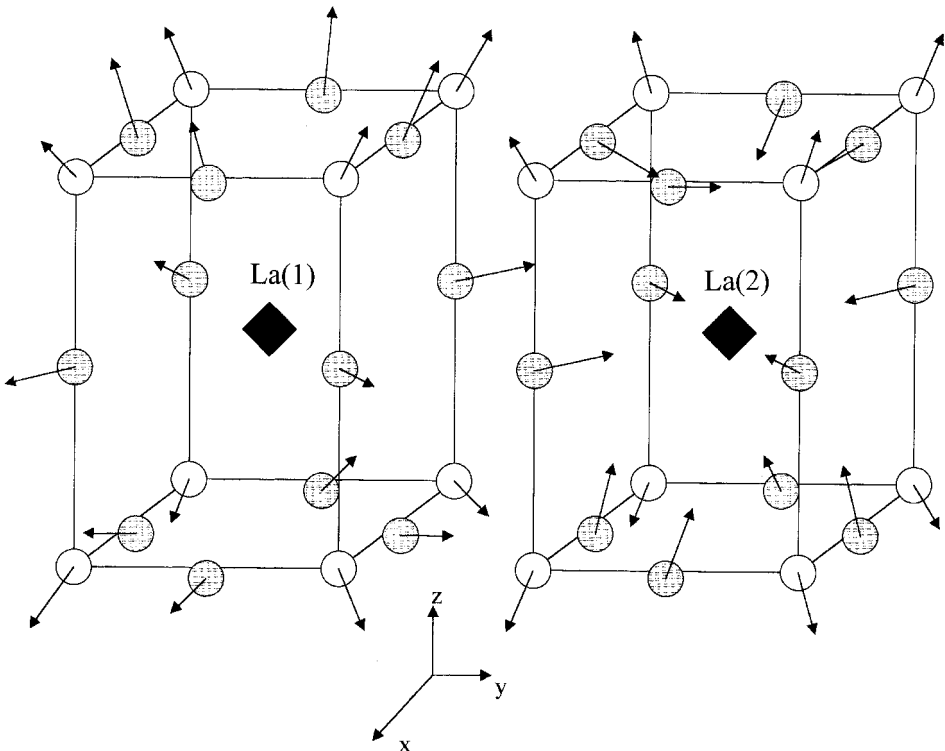


Figure 6. Schematic diagram of the atomic relaxation in the LUC of 160 atoms in the singlet state of the tetragonal phase.

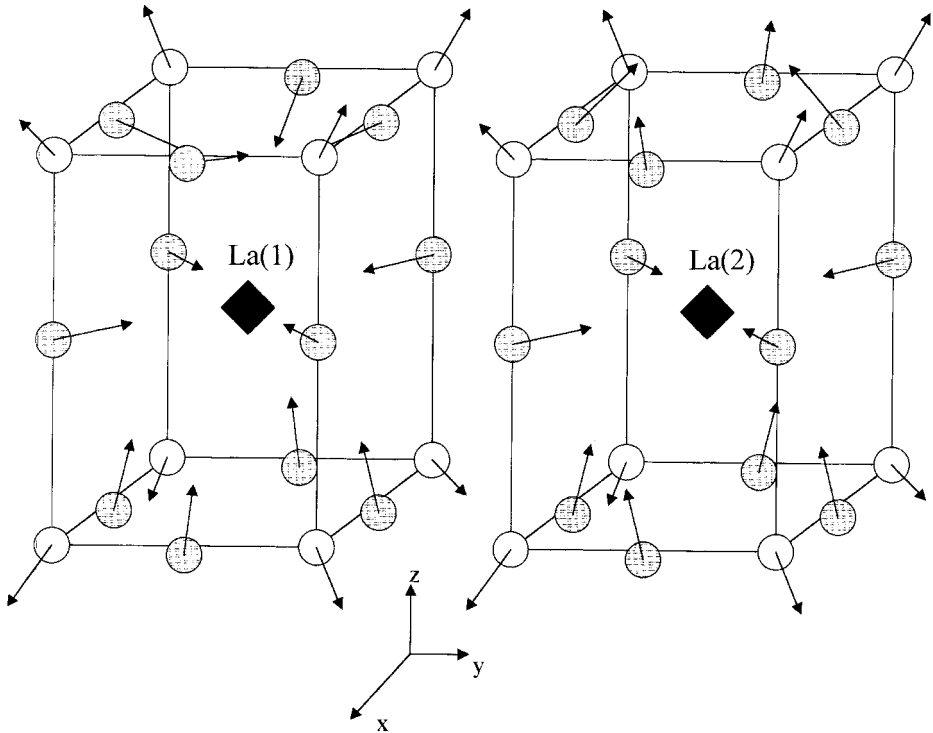


Figure 7. Schematic diagram of the atomic relaxation in the LUC of 160 atoms in the triplet state of the tetragonal phase.

intensity of the metallic peak, which is the triplet state according to our theory, with increasing La concentration.

### 3.5. Superconductivity and electron transfer

Our main objective is to try to describe the occurrence of the superconductivity in the  $\text{SrTiO}_3$  crystal when doped with La impurities. Below we shall try to analyse the most important results of this work with reference to the electronic properties and superconductivity phenomenon, which occur as a result of the La doping. The asymmetry in the relaxation of the atoms for both phases and states might explain the preference of one arrangement of the impurities instead of another. The transfer of the extra electrons is present for two arrangements of impurities,  $\langle 110 \rangle$  and  $\langle 101 \rangle$ , and just in the triplet state. This indicates that just the triplet state of the system is responsible for producing free electrons in the CB of the material and promoting the superconductivity. This is because the extra electrons transfer to the Ti 3d AOs, that is to the lower part of the CB. The Ti atoms receiving the electrons are situated in the Ti-O planes perpendicular to the ferroelectric  $z$  axis. We think that this indicates preferred planes where one can observe the superconductivity. Because in the singlet state the electrons are transferred from one La atom to another, it does not support the occurrence of superconductivity. This effect might be explained by spin attraction between the two electrons forming the singlet state. It is important to emphasize that the extra electron transfer to the CB *never* occurs in the cubic phase.

In order to give a possible first approximation for the explanation of superconductivity in SrTiO<sub>3</sub> and other ceramic materials, we should analyse the following aspects of these materials: firstly, their similarity in structure, which can be an important part of the theory, and, secondly, the rigidity of the crystalline lattice. As is known, any crystal has defined oscillation frequencies, which produce the macroscopic effect of heat in the crystal. Consequently, if the temperature of the crystalline lattice is very low, for example 14 K for SrTiO<sub>3</sub>, the oscillation frequencies will be widely separated.

However, this is not enough to explain the superconductivity. Our calculations have shown the existence of free electrons within the crystal due to the inclusion of the donor impurity. The free electrons before the application of an electric field are in thermal equilibrium with the crystal. Therefore, at low temperatures they will not have enough energy to excite the crystal to the next oscillation frequency. This thermal energy of the electron should be smaller than the difference between the two oscillation levels of the material at a given temperature. If this is the case, then free electrons will move through the material without resistance.

#### §4. CONCLUSIONS

We have presented a computational study of La impurities in a SrTiO<sub>3</sub> crystal considering both the cubic and the tetragonal structures of this material. The computations indicate that the La impurity can act as the centre of a new phase. When two La atoms are inserted instead of two Sr atoms we can anticipate the occurrence of two different states of the system: a singlet state when both extra electrons occupy the same local energy level within the bandgap and a triplet state when each extra electron occupies its own local energy level. The important outcome of our studies is that, for some La arrangements in the triplet state of the tetragonal phase, the extra electrons transfer to the CB. Thus one can expect an increase in the number of free charge carriers, which can contribute to superconductivity. This is in good agreement with the experimental studies showing the occurrence of superconductivity below 14 K in a La-doped SrTiO<sub>3</sub> crystal (Aiura *et al.* 1996, Suzuki *et al.* 1996). Furthermore, the extra electrons transferred to the CB are found to be situated on the Ti atoms forming Ti–O planes which are perpendicular to the *z* axis. This result is similar to that observed in the high-temperature cuprate superconductors (Myers 1997); so our conclusion is that the superconductivity in titanates and cuprates has the same origin and can be explained within the same theoretical model.

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