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A tight-binding model of the oxygen-vacancy in $SrTiO_3$

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Abstract. Using a tight-binding parametrisation of the band structure of $SrTiO_3$ together with the Green functions method, we calculate the energy levels of the oxygen vacancy. We show the ionic character of this defect and compare our results with previous calculation and experiments. We suggest an instability of the neutral and singly ionised vacancy with respect to polaron formation.

1. Introduction

Strontium titanate has been of considerable theoretical and experimental interest recently because of its unusual properties. The photochromic behaviour (Faughnan and Kiss 1968) has favoured many electronic studies: some of them concern surface properties such as photoemission (Henrich *et al* 1978), or structural phase transitions, others concern defect studies, such as EPR investigations in the IBM Zurich Laboratory (von Waldkirch *et al* 1972, Serway *et al* 1977). There have also been numerous theoretical investigations. Since the pioneering band structure calculation of Kahn and Leyendecker (1964), the APW calculations of Mattheiss (1972) and the simplified π band model of Wolfram (1972) and Ellialtioglu and Wolfram (1977) are basic ones. These calculations show that if strontium is completely ionised, there are strong covalent bonds between the d orbitals of titanium and the p orbitals of oxygen.

The purpose of the present work is to provide a theoretical calculation, along the line of these two authors, of the electronic states of the oxygen vacancies generally contained in $SrTiO_3$ samples. We use a tight-binding description of the band structure of the perfect crystal similar to those introduced by Mattheiss and Wolfram. The defect is introduced through the Green function formalism (Pantelides 1978). An approximate treatment of charge self-consistency allows the various charge states of the defect to be considered.

The scheme of the paper is as follows: in § 2, we show, on the simple semi-analytical model of Wolfram, how oxygen vacancy levels appear in the gap. § 3 is devoted to a more elaborate model, including second-neighbour interactions, based on the continuous fraction development of the Green functions given by Haydock *et al* (1972). A rough estimate of the effect of relaxation on the level position is also given. In § 4 we discuss the results and compare them with experimental data and other calculations.

2. First-neighbour interaction model

2.1. Structure

$SrTiO_3$ has the cubic perovskite-type structure shown in figure 1. We construct the nine upper valence bands and the five lower conduction bands from three p orbitals on each oxygen atom and five d orbitals on titanium as in APW calculations (Mattheiss 1972).

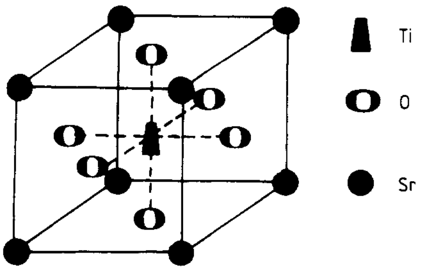

Figure 1. Atomic structure of $SrTiO_3$ in cubic perovskite-type symmetry.

Empty energy bands associated with the Sr ion are much higher in energy, while the occupied ones are much lower, so that it can be safely assumed that they may be disregarded in the calculation. The strontium ion is completely ionised, giving its two valence electrons to oxygen and titanium.

In this section we use the first-neighbour interaction model of Wolfram, which has the advantage of being semi-analytic. In this model, π and σ bands are uncoupled (Ellialtioglu and Wolfram 1977).

2.2. π bands

The two-dimensional π bands of $SrTiO_3$ are described by three parameters: $E_{p\pi}$, the diagonal energy of the bands on oxygen, $E_{d\pi}$, the diagonal energy of the t_{2g} bands on titanium, and $I_{pd\pi}$, the transfer integral between oxygen and titanium.

Note that, due to the high symmetry around the first-neighbour bonds, the first-neighbour interactions are reduced to a single parameter $I_{pd\pi}$.

The trace of the Green operator $G_\pi(E) = \lim_{\eta \to 0^-} (E - H_\pi + i\eta)^{-1}$ can be calculated analytically as shown by Wolfram (figure 2). Note the δ peak in the density of states which is characteristic of a first-neighbour model.

We next obtain the diagonal matrix elements of the Green operator for the p and d orbitals. Using symmetry properties, we get from $(E - H)G = 1$ the two relations:

$$(E - E_{d\pi})G^{xy}_{xy} - 4I_{pd\pi}G^{px}_{xy} = 1$$

$$(E - E_{p\pi})G^{px}_{px} - 2I_{pd\pi}G^{px}_{xy} = 1.$$

Together with the trace definition:

$$(1/N)\mathrm{Tr}\, G_\pi(E) = 2G^{px}_{px} + G^{xy}_{xy}$$

these relations allow us to obtain G^{px}_{px} and G^{xy}_{xy} analytically (figure 4). From these, the partial density of states of oxygen and titanium can then be calculated.

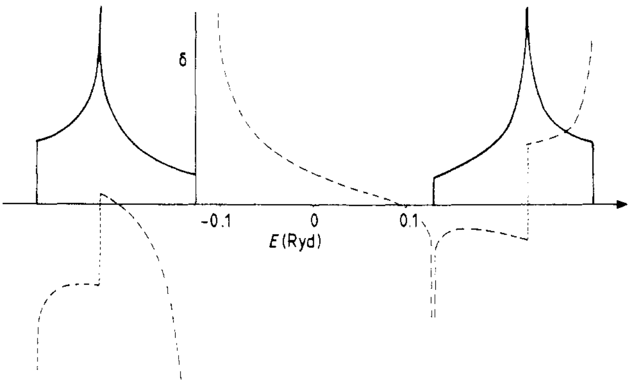

Figure 2. Density of states of the π bands for the analytical model of Wolfram. The broken curve shows the real part of the total Green function.

2.3. σ bands

As for π bands, the σ bands are described by three parameters $E_{p\sigma}$, $E_{d\sigma}$ and $I_{pd\sigma}$. But in this case the density of states cannot be calculated analytically. It is given approximately by Wolfram. We found it convenient to parametrise this form with a half ellipse and two linear segments, from which the real part of the Green function can be obtained analytically using the dispersion relation:

$$\mathrm{Re}\, G_\sigma(E) = -\frac{1}{\pi} P \int \frac{\mathrm{Im}\, G_\sigma(E)\, \mathrm{d}E'}{E - E'}.$$

The result for $SrTiO_3$ is represented in figure 3. As in § 2.2, the diagonal matrix elements

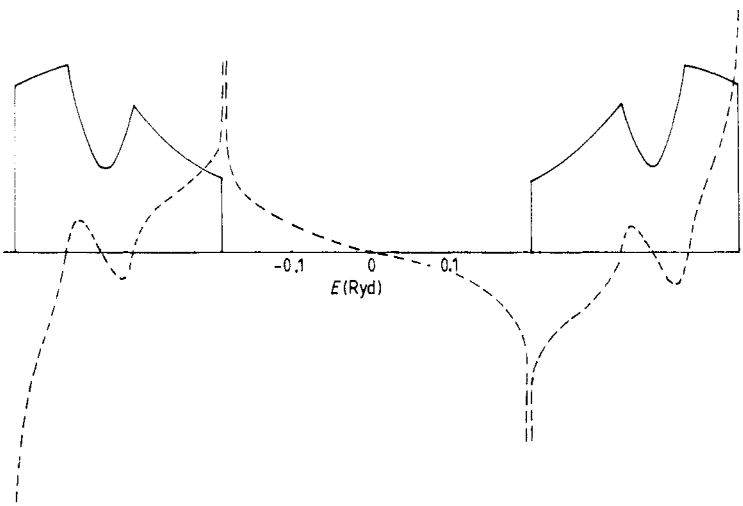

Figure 3. Density of states of the σ bands deduced from Wolfram. The broken curve shows the real part of the total Green function.

of the Green operator can be deduced from the relations:

$$(E - E_{d\sigma})G^{3z^2-r^2}_{3z^2-r^2} - 3I_{pd\sigma}G^{pz}_{3z^2-r^2} = 1$$

$$(E - E_{p\sigma})G^{pz}_{pz} - 2I_{pd\sigma}G^{pz}_{3z^2-r^2} = 1$$

$$3G^{pz}_{pz} + 2G^{3z^2-r^2}_{3z^2-r^2} = (1/N)\,\mathrm{Tr}\,G_\sigma(E).$$

The total effective charge on each atom is easily calculated from these diagonal matrix elements and is found equal to $-1.32|e|$ on the oxygen atom and $+1.96|e|$ on the titanium atom.

2.4. Oxygen vacancy

To remove the oxygen atom from the site labelled O, we put an infinite repulsive potential V_1 on the site (Pêcheur *et al* 1977). The vacancy levels are then given by the Dyson equation $\det(1 - G^0V_1) = 0$ for $V_1 \to \infty$, that is $G^{px}_{px} = 0$ and $G^{pz}_{pz} = 0$. The resonances are found in the conduction band, and no level appears in the gap, since no zeros of the real parts of G^{px}_{px} and G^{pz}_{pz} are found in the gap. This is shown in figure 4 for G^{px}_{px}.

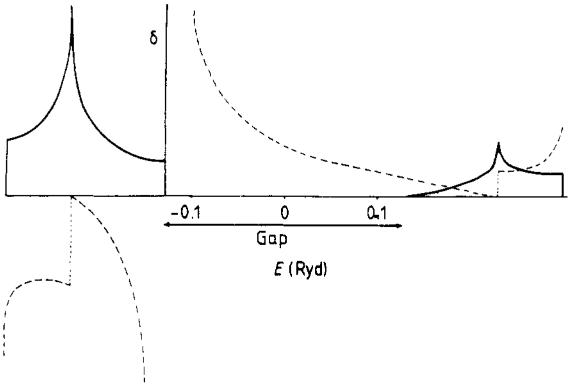

Figure 4. Partial density of states corresponding to the imaginary part of G^{px}_{px}. The broken curve shows the real part of this Green function.

To introduce some charge self-consistency in our calculation, a diagonal potential V_2 is introduced on the first neighbours and determined from a local neutrality argument. From the charge point of view, the oxygen vacancy appears in the crystal as an extra $+1.32|e|$ on an anion site. The local neutrality condition consists in choosing V_2 such that this extra charge is screened by an increase in the electron number on the first neighbours (Pêcheur *et al* 1979). This can be justified by noting that the extra charge must be screened by the electrons in a proportion given by the ε_∞ ($\sim$5) dielectric constant, which means that 80% of it is compensated by electronic charge. Moreover this screening is very short-ranged. The Thomas–Fermi screening length for the valence band electrons is 0.45 Å, a quarter of the nearest-neighbour distance (1.95 Å). One could then choose V_2 on the first neighbours to screen 80% of the vacancy charge. However this would neglect the effect of the remaining long-range screened Coulomb interaction on the impurity wavefunction, which extends on further neighbours of the vacancy. In the case of a charged vacancy in silicon, this term has been calculated by perturbation theory by Baraff and Schlüter (1978), in their density functional formalism. It is found to be less important than the short-range interaction for the impurity level position, but not negligible. In a simple semi-empirical scheme we have preferred to choose V_2, so as to have complete screening (local neutrality) on the first neighbours. This compensates somehow for the neglect of long-range interactions and works satisfactorily in the case of the silicon vacancy when compared with the complete density functional calculation of Baraff and Schlüter (Kauffer *et al* 1977). In the present case, it presumably overestimates the effects of the long-range screened interaction (leading to levels slightly too low) since this long-range interaction itself must be efficiently screened by the ion displacements in a material with such a high value for the static dielectric constant ε_0 ($\sim$320). Note that the value of V_2 satisfying the local neutrality depends on the impurity level occupancy so that one can calculate the influence of the charge states of the vacancy on the position of the levels.

The Dyson equation now contains V_1 and V_2 and we also need the Green functions on the two Ti neighbours of the vacancy.

Two of them of symmetry E_g and E_u can be calculated analytically using recursion relations like those used for G_{px}^{px} and G_{pz}^{pz}. The other Ti Green functions are calculated with the continuous fraction method (Haydock *et al* 1972) of the form

$$G(E) = \frac{1}{E - a_1 - b_1 g_1(E)}$$

where

$$g_1(E) = \frac{1}{E - a_2 - b_2 g_2(E)}$$

and so on.

The usual single level termination for the continuous fraction gives numerous extra peaks in the density of states. Nevertheless, in this case, each level i of the development describes alternatively metal or oxygen neighbours sheets, and the a_i are alternatively $E_{d\pi}$ or $E_{p\pi}$ for the π bands ($E_{p\sigma}$ or $E_{d\sigma}$ for the σ bands). So, we use a two-level termination at level n, which is defined by

$$T = \frac{1}{(E - a_1)(E - a_2) - (b_{n-2} + b_{n-1}) - b_{n-1} b_n T}.$$

(The values of b_i are also different for π and σ bands.) We thus obtain a good description of the valence and conduction bands (except for an inessential widening of the δ peak).

For different charge states of the vacancy (that is, for various occupancies of the localised state) localised levels do appear in the gap (see table 1).

The lowest level possesses E_g symmetry, but an E_u level also appears with a slightly higher energy. A study of the analytical form of the E_u and E_g Green functions shows that, for E_g symmetry, the real part of the Green functions diverges logarithmically at the conduction band edge and localisation falls to zero at this point. This is related to the discontinuity of partial density of states (imaginary part of the Green function) at the conduction band edge (see figure 2). For E_u, there is no singularity at the bottom of the conduction band and localisation varies only slowly when the level crosses the band edge.

Table 1. Bound levels obtained for different charge states for oxygen vacancy with first-neighbour approximation. E_{cb} is the energy for the bottom of the conduction band. Energies are in Rydbergs.

Charge	Level population	Potential	Level position $E_{cb} - E_l$	Level localisation
0	2 electrons	−0.051	0.0085	0.545
+1	1 electron	−0.087	0.0313	0.676
+2	0 electrons	−0.120	0.0539	

3. Second-neighbour approximation

3.1. *Perfect crystal*

A better representation of the valence band is obtained with the introduction of interactions between neighbouring oxygen atoms. Their major effect is to broaden the δ function located at the top of the valence band, and corresponding to non-bonding flat bands in the first-neighbour model.

For simplicity, we have treated the second-neighbour interaction in the two centre approximation, retaining only the $I_{pp\sigma}$ parameter. (Symmetry considerations would allow up to six independent parameters for the second-neighbour oxygen–oxygen interactions, as shown in table 2.) This allows a good description of the band structure of

Table 2. LCAO parameters obtained for the two approximations used in this work. Energies are in Rydbergs.

Integral	Two-centre approximation	First-neighbour model	Second-neighbour model
$E_{xx}(0,0,0)$	$E_{p\sigma}$	−0.128	−0.1582
$E_{yy}(0,0,0)$	$E_{p\pi}$	−0.128	−0.1582
$E_{xy,xy}(0,0,0)$	$E_{d\pi}$	0.128	0.128
$E_{3z^2-r^2,3z^2-r^2}(0,0,0)$	$E_{d\sigma}$	0.305	0.305
$E_{x,xy}(0,\frac{1}{2},0)$	$I_{pd\pi}$	0.096	0.096
$E_{z,3z^2-r^2}(0,0,\frac{1}{2})$	$I_{pd\sigma}$	−0.156	−0.156
$E_{x1,x2}(\frac{1}{2},\frac{1}{2},0)$	$\frac{1}{2}(I_{pp\sigma}+I_{pp\pi})$	0	0.0117
$E_{x1,y2}(\frac{1}{2},\frac{1}{2},0)$	$\frac{1}{2}(I_{pp\sigma}-I_{pp\pi})$	0	0.0117
$E_{x1,x2}(\frac{1}{2},\frac{1}{2},0)$	$\frac{1}{2}(I_{pp\sigma}-I_{pp\pi})$	0	0.0117
$E_{z1,z2}(\frac{1}{2},\frac{1}{2},0)$	$I_{pp\pi}$	0	0

Mattheiss with only seven parameters, although we still neglect the contribution of s bands, the interaction between metal atoms, and the π interaction between oxygen atoms, which is smaller than the σ ones.

The density of states is determined using the continuous fraction method in a cluster of 5745 atoms, with 15 coefficient pairs. Here also the usual continuous fraction termination cannot be used because, as in the first neighbours model, the two-dimensional property of π bands in perovskites gives a slow convergence of the coefficients a_i and b_i of the continuous fraction. A one-level termination after 15 terms creates numerous extra peaks in the density of states.

We then use the δ function representation of Gordon (1968). This can be described briefly as follows: given a starting vector α, the Haydock recursion scheme leads to a tridiagonal $N \times N$ matrix representation for the Hamiltonian. This matrix is then diagonalised to obtain N eigenvalues ε_i and N eigenvectors a_i^j. The Green function is then given by:

$$\mathrm{Re}\, G_{\alpha,\alpha}(E) = \frac{1}{N}\sum_i \frac{|a_i^\alpha|^2}{E - \varepsilon_i}$$

and

$$\mathrm{Im}\, G_{\alpha,\alpha}(E) = -\frac{\pi}{N}\sum_i |a_i^\alpha|^2\, \delta(E - \varepsilon_i).$$

A gaussian broadening is then performed to obtain the density of states shown in figure 5 (with $\Gamma = 0.02$ Ryd). The total effective charge on each atom is $-1.42|e|$ on the oxygen and $+2.26|e|$ on the titanium.

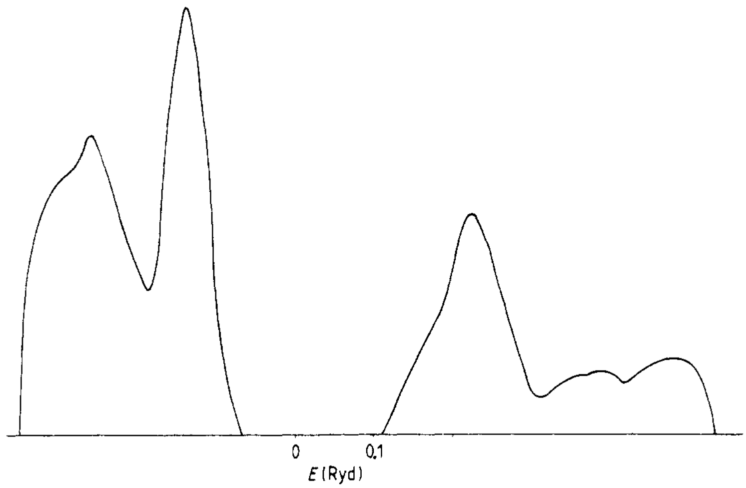

Figure 5. Density of states obtained in the second-neighbour interaction model, with continuous fraction method and gaussian broadening of 0.02 Ryd of the δ functions obtained with the Gordon representation.

3.2. *Oxygen vacancy*

In this more complicated model, we perform the vacancy calculation directly in the perturbed crystal (with a removed oxygen atom). This is possible since the recursion method does not require periodicity.

In the perovskite structure, the oxygen vacancy has only two nearest neighbours (Ti atoms) and the local neutrality condition as used before may be too strong. So we include the eight second neighbours (O atoms) in the self-consistency domain (with a diagonal perturbation potential V_3). To keep a single parameter we use $V_3 = V_2/\sqrt{2}$ (which would correspond to a coulombic perturbation potential).

Proceeding as before, we obtain the results of table 3.

Table 3. Bound levels obtained for different states of charge for oxygen vacancy, with second-neighbour approximation. E_{cb} is the energy for the bottom of conduction band. Energies are in Rydbergs.

Charge	Level population	Potential	Symmetry	Level position $E_{cb} - E_l$	Localisation
0	2 electrons		E_g		
+1	1 electron	−0.08	E_u	0.03	0.71
			E_g	0.02	0.68
+2	0 electrons	−0.16	E_u	0.093	0.71
			E_g	0.079	0.71

3.3. *Effects of lattice relaxation*

The relaxation of the atoms around the vacancy may be expected to change the level positions as calculated before. No first-order Jahn–Teller effect exists, so we consider only a radial relaxation around the vacancy. To get an estimate of the effect of this lattice relaxation on the level position, we have proceeded in the following way. First we displace only the first neighbours of the vacancy, since these displacements have a major influence on the level position, owing to the localisation of the vacancy state on these first neighbours. Then we only take into account the change in the first b in the continuous fraction of § 2.4, which is the most important effect of the relaxation. This b_1 for the E_u symmetry (which contains the occupied level) is given by:

$$b_1 = \tfrac{1}{2}\sum_{1}^{6} (I_{pd\pi})^2,$$

where the summation is extended over six oxygen first neighbours of the two titanium atoms around the vacancy. (The π orbitals of titanium atoms are only coupled to the p orbitals of six of their ten oxygen neighbours). For not too high displacement values, only coupling to the two oxygens on the titanium atom line are appreciably modified; we chose for these a variation with the distance d of $d^{-7/2}$, as proposed by Harrison (1980). The results found for relaxation of 5% and 10% of the first neighbour distance are shown in table 4. The level is slightly lowered when the titanium moves towards the vacancy and rises up close to the conduction band bottom when the titanium atoms move away from the vacancy.

Table 4. Effect of the relaxation of the titanium atoms around the O vacancy on the localised E_u level for the singly ionised vacancy. ΔE is the variation of the level energy in Rydbergs.

d(Å)	$\Delta d/d$(%)	$I_{pd\pi}$	ΔE	Localisation
2.147	+10	0.0687	0.0094	0.76
2.05	+5	0.0809	0.0055	0.74
1.952	0	0.096		0.71
1.855	−5	0.115	0.0076	0.69
1.757	−10	0.139	0.018	0.64

4. Discussion

For the neutral and singly ionised vacancy the potential values and the positions of the energy levels are quite similar in the two models. In model 2, it is not possible to perform self-consistency for the neutral vacancy, but it is known from the first-neighbour model that an E_g level in the upper part of the gap appears for any small attractive potential (on account of the discontinuity of the density of states). The continuous fraction expansion is not appropriate to treat these shallow levels, which do not appear clearly in the δ function representation of Gordon.

For the doubly ionised vacancy, a greater value of potential is needed in model 2 and the level is lower than in model 1. Moreover the lower state is not always E_g and becomes E_u for the more attractive potentials.

Both models show that the oxygen vacancy is an ionic defect: it is only the potential V_2 (and V_3) due to the charge effect which is responsible for the existence of localised levels in the gap.

The main conclusion of this calculation is that the occupied energy levels associated with the oxygen vacancy (neutral and singly ionised) are not very deep. Even the singly ionised vacancy level has a binding energy of only 0.03 Ryd (table 3) which is close to usual polaron energies for transition metal oxides. For instance, a polaron energy of 0.025 Ryd has been reported for WO_3 (Schirmer and Salje 1980). This might well mean that the singly ionised (and neutral) vacancy is unstable with respect to polaron formation. This would be in line with the experimental results of Yamada and Miller (1973), who found only doubly ionised vacancies in reduced strontium titanate even at low temperatures. This is also consistent with the interpretation of UV photoemission and electron energy-loss spectroscopy experiments given by Henrich *et al* (1978), who attributed the gap states to surface rather than bulk defects.

Our results are qualitatively different from those of Tsukada *et al* (1980), who performed X_α calculations for the oxygen vacancy in $SrTiO_3$. These authors found a rather deep level for the neutral vacancy. As shown by them, this level originates from a $d_{3z^2-r^2}$ orbital interacting with a $4p_z$ excited state through the electric field of the vacancy, so that a σ state is lowered into the middle of the gap. These results for the neutral vacancy appear to disagree with the experiments of Yamada and Miller (1973). A possible explanation is that the very small cluster Ti_2O_{11} used by Tsukada *et al* gives a bad description of the excited 4s–4p states of $SrTiO_3$ in terms of the localised molecular $4p_z$ orbitals. This would lead to a strong overestimate of their coupling with the $d\sigma$ conduction states. In our calculation, these 4s–4p have been neglected since they cannot be described correctly in a tight-binding scheme and since they are expected, owing to their delocalisation, to be much less sensitive to the vacancy potential than the d orbitals. As a consequence, the σ states only contribute to resonances which are found in the π conduction band, but do not appear in the band gap.

As far as the relaxation is concerned, we first note that the relaxation of the Ti atom around an oxygen vacancy is not experimentally known. From EPR results, Siegel and Müller (1979) have deduced a model of the structure of transition-metal-impurity–oxygen-vacancy pair centre in $SrTiO_3$. They conclude that Fe^{3+} and Mn^{2+} move by 0.2 Å towards the neighbour vacancy (10% of the perfect crystal distance). On the other hand in TiC_{1-x} and NbC_{1-x}, which are metallic compounds of NaCl structure, the metal first neighbours of the vacancy move away from the vacancy site by about 4% of the perfect-crystal nearest-neighbour distance (Moisy-Maurice *et al* 1981). We then expect the relaxation around the vacancy to be rather weak (of a few per cent). From our results in § 3.3, its influence on the level position should be insufficient to alter the preceding conclusions. Note that we did not attempt to estimate the effects of relaxation on the formation energy of the defects. For this, we would have to take into account the energy changes in the valence band, as well as taking into account the double counting of the electronic interaction terms.

5. Conclusion

Our results for the oxygen vacancy in $SrTiO_3$ obtained with a tight-binding model lead to a defect having an ionic character and to occupied levels close to the conduction band (for neutral and even the singly ionised vacancy). This favours the instability of these two charge states with respect to polaron formation and could explain the experimental observation of doubly ionised vacancy down to very low temperatures.

The present method can be extended to other defects, or associations of defects. It has its own drawbacks (such as the approximation in the self-consistency treatment) but is devoid of any cluster approximation and can be expected to be a useful alternative to the X_α calculation. Its relative simplicity should be appreciable, in particular in the treatment of associated centres such as those described by Siegel and Müller (1979).

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