Ab initio study of a TiO$_2$/LaAlO$_3$ heterostructure

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Abstract.
In this work we explore the origin of the ferromagnetism appearing when a TiO$_2$ film is grown on another non-magnetic oxide as a substrate such as LaAlO$_3$ (001), concentrating on the role played by the oxygen vacancies in this phenomenon. Using Density Functional Theory ab-initio methods, we study the free-standing anatase film as well as the interfaces with either the LaO or AlO$_2$ planes of LaAlO$_3$. Our results show that the interface LaO/TiO$_2$ is favored against the AlO$_2$/TiO$_2$ one if no oxygen vacancies are present in the interface whereas the contrary happens when there are oxygen vacancies. In both cases, the cohesive energy is of the same order of magnitude but only at AlO$_2$/TiO$_2$ we found a magnetic solution.

1. Introduction
Intense search for ferromagnetism above room temperature in dilute magnetic semiconductors and insulators has taken place in recent years. The fabrication of these materials offers exciting possibilities for spintronics and the use of wide gap oxides is appealing for magneto-optical devices. Room-temperature ferromagnetism has been observed in both doped [1] and undoped insulating oxide thin films such as TiO$_2$, ZnO and HfO$_2$ [2, 3] grown over other oxides or semiconductors. This magnetic order can be weak and the determination of its intrinsic character may require complementary, independent and careful techniques to be probed [4, 5]. Many authors have attributed an important role to oxygen vacancies [6, 7] and other defects [8] to produce this magnetic ordering, but the effect of the substrate or the interface has not been taken into account in the interpretations.

Considering the open questions in the aforementioned systems, in this work we explore the possibility of observing magnetism in an heterostructure formed by a simple oxide such a TiO$_2$ anatase and a LaAlO$_3$ (LAO) substrate. Experiments show that large terraces are formed on the substrate surface, and that the growth is epitaxial on the (001) direction [9]. However, it is not clear if the surface is mostly composed of LaO planes or of AlO$_2$ planes [10, 11]. Spectroscopic experiments show that there are mixed-valence Ti ions in these films, which may be due to the presence of oxygen vacancies [12]. The magnitude of the magnetization has been found to be proportional the oxygen content in some experiments [13]. We therefore concentrate on the effect of oxygen vacancies in the electronic structure and in the interfacial structural relaxation, as the electric fields due to the dipole layer at the interface may lead to important changes in the positions of the atoms with respect to the bulk materials. For this purpose we perform ab-initio calculations for the two interfaces in a TiO$_2$/LAO heterostructure using computational codes such as SIESTA [14] or Wien2k [15] and also different unit cells.
We first study separately the component systems: TiO$_2$ and LAO in bulk and as free standing slabs, representing the deposited anatase film and the substrate, respectively. As the ab-initio codes allow only the study of three dimensional periodic systems, the films are represented by repeated slabs with enough free space between them. For the heterostructure, two different types of unit cell were used: trilayer slabs LAO/TiO$_2$/LAO and superlattices TiO$_2$/LAO/TiO$_2$/LAO...

The calculations are performed within the density functional theory (DFT) [16] using the full potential augmented plane waves method, as implemented in the Wien2k code [15]. We use the local density approximation (LDA) [17] for the exchange and correlation, and small muffin tin radii to allow for lattice relaxation. The muffin tin radii used were $R_{MT_{Ti}} = 1.7$ bohr, $R_{MT_{O}} = 1.4$ bohr, $R_{MT_{La}} = 2.5$ bohr, $R_{MT_{Al}} = 1.7$ bohr. The number of plane waves in the interstitial region is mostly restricted to $R_{KMax}=6$ although in many cases it was increased to $R_{KMax}=7$ and no qualitative difference was observed. The effect of increasing the number of k-points was also checked.

2. TiO$_2$ anatase and LAO: Bulk and surface properties

TiO$_2$ anatase and LAO are both conventional band insulators, with in-plane bulk lattice parameter $a=3.79$ Å [18] (Fig. 1). The small mismatch between the in-plane lattice constants allows for a good epitaxial experimental outcome [9].

TiO$_2$ anatase presents a 3.2 eV band gap between filled oxygen 2p bands and unfilled Ti 3d conduction bands. The calculated band gap is 2.2 eV as shown in Fig. 2(a). When oxygen vacancies are formed in the bulk anatase structure the calculations show that the system becomes metallic and a vacancy level appears inside the gap, very close to the conduction band. The small band gap and the vacancy levels very close to the conduction band are well known features of the LDA approximation.

LAO presents a 5.6 eV gap between filled O-2p bands hybridized with Al-p states and unfilled conduction bands composed mostly of La-4f states. The calculated gap is 4 eV, as shown in Fig. 2(b).

![Figure 1](image1.png)

**Figure 1.** Bulk unit cells of the two component systems. The arrows on the oxygen atoms in the anatase structure indicate that they are off-plane.

![Figure 2](image2.png)

**Figure 2.** Density of States of: (a) bulk TiO$_2$ anatase, (b) bulk LAO (c) and (d) Superlattices either with AlO$_2$ or LaO planes in the interfaces (relaxed structures).
shape under relaxation, which is not possible with the Wien2k code. This results in a strong deformation of the (001) surface, that goes from a square into a rectangular shape, and also makes the slab thinner. The free standing anatase film would therefore deform in that way, but as we are studying its epitaxial growth over LAO we keep the in plane lattice constant fixed and the cell shape square. Relaxation is only considered in the z direction, perpendicular to the slab. With this constraint we create oxygen vacancies in the surface of the slab and relax the atomic positions using the Wien2k code. The vacancies seem to be crucial for the appearance of magnetism: on one hand, magnetic solutions appear if there are oxygen vacancies at the surface and on the other hand the value of the magnetic moment increases with the number of vacancies. In our calculations, one vacancy per surface cell (50%) gives after relaxation a magnetic moment of 0.3 $\mu_B$, localized at the Ti atom in that surface, while two vacancies per surface cell give 2 $\mu_B$. In Fig. 3 we show the charge and spin density maps near the surface for the anatase slab with two vacancies per surface (all the surface oxygen atoms removed). The system is clearly magnetic, and the magnetic moment is mostly localized in the Ti superficial atom.

The other building block of the heterostructures is the slab of LAO. Along the (001) direction this slab alternates layers of AlO$_2$ (negatively charged) and LaO (positively charged). Therefore, an integer number of unit cells in the z direction would produce a large dipole and it is more convenient to use an odd number of layers. For the superlattices we consider 5 layer slabs with either LaO or AlO$_2$ termination. In both cases the system becomes metallic within the LDA approximation and the interesting change with respect to the bulk density of states, shown in Fig. 2(b), is that the LaO termination shifts the unoccupied surface La states substantially towards the Fermi energy.

![Figure 3](image-url-1)

**Figure 3.** Charge and spin density of the surface of a TiO$_2$ slab with no oxygen atoms at the surface.

![Figure 4](image-url-2)

**Figure 4.** Schematic diagram for the unit cell of one of the superlattices studied.

### 3. TiO$_2$/LAO superlattices

We perform calculations on superlattices like the one shown schematically in Fig. 4. We have considered the 2 cases: the TiO$_2$ plane facing the AlO$_2$ or the LaO termination. In both situations we assume that the oxygen atoms of the LAO surface face the Ti atoms of the anatase surface. The lateral lattice parameter is kept fixed at the experimental value for LAO but the distance between the two slabs composing the heterostructure is obtained by minimizing the total energy. The fact that the total energy has a minimum when changing this distance verifies that there is bonding between the two materials and also gives the optimal value for that distance. This fixes the size of the superlattice unit cell along the z axis for each case. Afterwards, all the atoms are allowed to relax until the force on each one is less than 2 mev/Å.
We find that there is a competition between the tendency of the anatase film to shrink (as in the free standing slab) and the tendency to bond to LAO. In particular, if an oxygen from the anatase surface faces an Al atom the bond is strong.

Fig. 2(c) and (d) show the density of states of the two superlattices without vacancies and after relaxation. Both interfaces are metallic without vacancies. This metallicity is not altered by the formation of oxygen vacancies or by structural relaxation.

Due to the anatase structure there are two types of AlO$_2$/TiO$_2$ interfaces. This can be inferred from Fig. 1 and Fig. 4, but it is shown more clearly in Fig. 5. To simulate growth conditions in a typical experiment [19], we introduced oxygen vacancies at both layers of the interface and found that it is more favorable to perform them in the TiO$_2$ layer rather than in the AlO$_2$ plane.

We find magnetic solutions in the unrelaxed geometry, with and without vacancies, but the magnetic moments decrease with structural relaxation. Without vacancies the moments are located in some of the oxygen atoms and disappear with relaxation. With vacancies they are located in the Ti superficial atoms and do not disappear.

Fig. 6 shows the charge and spin densities of the superlattice, when there are no oxygen atoms in the TiO$_2$ side of the interfaces. Although both interfaces have the same number of missing oxygen atoms, only one of them is magnetic, depending on the relative orientation of the second neighbor layers.

**Figure 5.** Charge density for the superlattice with AlO$_2$/TiO$_2$ interface without vacancies. Distance from the surface Al to the neighbor anatase oxygen is shorter in interface 1.

**Figure 6.** Charge (left) and spin (right) density maps for the system of Fig. 5 with 2 vacancies. Only one interfacial Ti ion is magnetic.

We also study the LaO/TiO$_2$ heterointerface and perform oxygen vacancies to simulate experimental growth conditions. Introducing vacancies in this case is less favourable compared to the other interface and magnetic solutions are only found with many oxygen vacancies present, as shown in Table 1.

The cohesive energy of a superlattice, given in Table 1, is obtained subtracting from its total energy the energy of the relaxed slabs of TiO$_2$ and LAO that compose it. The supercell with LaO/TiO$_2$ interface has more cohesive energy if no vacancies are present while the one
with AlO$_2$/TiO$_2$ interface is preferred if there are oxygen vacancies. This last case presents a magnetic moment, localized at the superficial Ti atom.

**Table 1.** Cohesive energies and total magnetic moments per unit cell for the two types of superlattices considered. The number of vacancies (vac) is the number of missing oxygen atoms from the anatase side of each interface.

| case | Ti/Al | Ti/La |
|------|-------|-------|
|      | E (eV) | µ ($\mu_B$) | E (eV) | µ ($\mu_B$) |
| no vac | 4.89 | 0.01 | 6.86 | 0 |
| 1 vac | 6.65 | 0.26 | 6.01 | 0 |
| 2 vac | 6.62 | 1.28 | 5.94 | 0.57 |

4. Conclusions

The calculated cohesive energies allow us to draw some conclusions referring to experiments where the TiO$_2$ film grows over a LAO substrate with terrace-like structure where there are both LaO and AlO$_2$ layers. When the film is in contact with the LaO layer, the magnetic atom will not be at the interface with the substrate but rather at the free surface of the anatase film. In that case, the role of the substrate would be just epitaxial, fixing the structure of the anatase film grown on it. If in turn the film is in contact with the AlO$_2$ layer, it is likely that oxygen vacancies occurring during the growth will be located at that interface and the Ti at the interface would be magnetic.

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