Magnetism in a TiO$_2$/LaAlO$_3$ heterostructure: an ab initio study about the role of oxygen vacancies

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In this work we study the electronic structure and magnetism of a TiO$_2$ film grown on another non-magnetic oxide such as a LaAlO$_3$ (001) substrate, concentrating on the role played by structural relaxation and oxygen vacancies. 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$_3$, focusing on the possibility of magnetic solutions. 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 the AlO$_2$/TiO$_2$ interface presents an stable magnetic solution.

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I. INTRODUCTION

The development of modern microelectronics devices requires the knowledge of the electronic structure near interfaces. In this respect, oxide materials combine many of the important properties of semiconductors and add novel phases such as metal-insulator transitions, superconductivity, quantum Hall effect, orbital reconstruction, colossal magnetoresistance, etc. One interesting phenomena reported recently is the change in the properties of complex oxides when they are arranged in a heterostructure. For example, LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) are both insulators and non-magnetic in their bulk form but one possible interface between them is conductive and ferromagnetic. The origin of the ferromagnetism and the conductivity is not known, it has been attributed to the polar discontinuity between the charged layer (LaO) in contact with the neutral layer (TiO$_2$), that would produce a transfer of electrons at the interface, and also to the presence of oxygen vacancies created during film growth.

The previous findings may be related to the recent intense search for ferromagnetism above room temperature in dilute magnetic semiconductors and insulators. The fabrication of these materials offers exciting possibilities for spintronic devices and the use of wide gap oxides is appealing for magnetooptical devices. In that direction, room-temperature ferromagnetism has been observed in both doped and undoped insulating oxide thin films such as TiO$_2$, ZnO and HfO$_2$ 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. Many authors have attributed an important role to oxygen vacancies and other defects 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 LAO substrate. Experiments show that large terraces are formed on the substrate surface, and that the growth is epitaxial in the (001) direction. However, it is not clear if the surface is mostly composed of LaO planes or of AlO$_2$ planes. XPS experiments show that there are Ti$^{+3}$ and Ti$^{+2}$ ions in these films, which may be due to the presence of oxygen vacancies or to the polar catastrophe. The magnitude of the magnetization has been found to be proportional the vacancy concentration in some experiments, for example in ref. We therefore concentrate on the effect of oxygen vacancies in the electronic structure and on the interfacial structural relaxation, as it is expected that 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, as it happens in other interfaces. For this purpose we perform ab-initio calculations for the different interfaces present in the TiO$_2$/LAO heterostructure using computational codes such as SIESTA or Wien2k 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 paper is organized as follows: In Sec. II we very briefly outline our calculational approach. In Sec. III we discuss the bulk and surface electronic properties of the component materials. In Sec. IV we present the results for the trilayers and superlattices and in Sec. V our conclusions.
II. CALCULATION DETAILS

The calculations are performed within the density functional theory (DFT)\textsuperscript{27} using the full potential augmented plane waves method, as implemented in the Wien2k code\textsuperscript{26}. We use the local density approximation (LDA)\textsuperscript{28} 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. In some cases we relax the structure with the Siesta code\textsuperscript{25} as it allows for further cell deformation.

III. TiO\textsubscript{2} ANATASE AND LAO: BULK AND SURFACE PROPERTIES

TiO\textsubscript{2} anatase and LAO are both conventional band insulators, with in-plane bulk lattice parameter \(a=3.79\)\textsubscript{Å}\textsuperscript{29} (Fig. 1). The small mismatch between these in-plane lattice constants allows for a good epitaxial experimental outcome\textsuperscript{21}.

FIG. 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 with respect to the Ti atoms.

TiO\textsubscript{2} anatase presents a 3.2 eV band gap between filled oxygen 2\(p\) bands and unfilled Ti 3\(d\) conduction bands. The calculated band gap is 2.2 eV as shown in Fig. 2a. 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 (Fig. 3). The small band gap and the vacancy levels very close to the conduction band are typical features of the LDA approximation.

LAO presents a 5.6 eV gap between filled oxygen 2\(p\) bands hybridized with Al 3\(p\) states and unfilled conduction bands composed mostly of La 4\(f\) states. The calculated
gap is 4 eV, as shown in Fig. 2b), and when oxygen vacancies are created in this system the calculated vacancy levels appear well inside the band gap.

Summing up, both materials are non-magnetic insulating oxides in bulk and if oxygen vacancies are present they keep their non-magnetic character although the electronic structure changes, as vacancy levels appear inside the band gap.

In order to get some insight about how these bulk properties change in the heterostructure, we study slabs of the component materials along the (001) direction. The anatase slab with 5 or 9 TiO$_2$ layers is used to model the properties of the free surface of an anatase film. A different DFT calculation, using the SIESTA code, allows the unit cell to change its shape under relaxation, which is not the case 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 (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 give 2 $\mu_B$. In Fig. 4 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 effect of structural relaxation is to move this Ti atom closer to the remaining oxygen neighbor, which is apical and in the subsurface layer, thus making the slab thinner. In fact, this distance decreases from 1.97 Å in bulk TiO$_2$ to 1.89 Å for a surface with no oxygen vacancies and to 1.75 Å if there are oxygen vacancies in the surface layer as in Fig. 4. In the slab with 5 TiO$_2$ layers the two surfaces interact in such a way that the magnetic moments are smaller than in the 9-layer slab.

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. 2b), is that the LaO termination shifts the unoccupied surface La states substantially towards the Fermi energy. This can give as a result a large hybridization with the unoccupied Ti states of TiO$_2$, but will not modify the occupied states.

IV. TiO$_2$/LAO SUPERLATTICES

The system we propose to study is a TiO$_2$ (001) film with anatase structure grown epitaxially over a LAO (001) substrate. For this purpose we perform calculations on the superlattices 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 unit cell we use consists of 5 layers of each material and contains 27 or 28 atoms. 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, for example we notice that it changes when there are oxygen vacancies. Afterwards, all the atoms are allowed to relax inside the unit cell 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. Also, there is an electrostatic effect due
to the charge in each layer of LAO, which is of course different for a neutral TiO$_2$ layer and for a charged layer, when oxygen vacancies are created in the anatase surface.

Fig. 2(c) and (d) show the density of states of the two superlattices without vacancies and after relaxation. These graphs give some insight about electron transfer or the possibility of oxygen vacancy formation, in agreement with experiments. In the case of the AlO$_2$/TiO$_2$ interface, the states readily available near $E_F$ are O-2p states. This interface will then be prone to the formation of oxygen vacancies in order to allow for a compensation of the polar discontinuity present at the interface. For the LaO/TiO$_2$ interface instead, the states near $E_F$ are mainly comprised of Ti 3d-states. This accessibility to a mixed valency of Ti allows for a transference of electrons across the interface to overcome the electrostatic potential divergence. Both interfaces are metallic without vacancies. This metalliclicity is not altered by the formation of oxygen vacancies or by structural relaxation.

A. AlO$_2$/TiO$_2$ heterointerface

Due to the anatase structure there are two types of AlO$_2$/TiO$_2$ interfaces. This can be inferred from Fig. 1 and Fig. 5(a), but it is shown more clearly in Fig. 6. To simulate growth conditions in a typical experiment, 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.

When the heterostructure is formed, the interface becomes metallic; with no oxygen vacancies the Fermi level lies in the valence band (Fig. 2(c)) and with vacancies it moves to the conduction band.

We find magnetic solutions in the unrelaxed geometry, with and without vacancies, but the magnetic moments decrease with structural relaxation as can be seen in Table 1. Without vacancies the moments are located in some of the oxygen atoms and disappear with relaxation. With vacancies they are located in the Ti super-ficial atoms and do not disappear, they only decrease somewhat. One particular example of the structural relaxation is shown in Fig. 7 indicating schematically how each of the atoms moves in the magnetic interface. The atom that has a larger displacement is the anatase oxygen facing Al, it bonds more strongly with Al than with Ti. Relaxation changes the buckling of the anatase surface.

FIG. 7: Schematic diagram showing the atomic relaxation on the magnetic interface (namely, interface 2 in Fig. 6) when there is one oxygen vacancy at the anatase surface. The movement of each atom (in Å) is indicated when it is significant (more than 0.05 Å)

Fig. 8 shows the charge and spin densities of the superlattice, when there are no oxygen atoms in the TiO$_2$
side of the interfaces (2 vacancies). Although both interfaces have the same number of missing oxygen atoms and first neighbours, only one of them is magnetic, depending on the relative orientation of the second neighbor layers. This points to the new result that magnetism is not only due to interactions between interfacial atoms but also further neighbours are important.

The corresponding density of states is shown in Fig. 9 where the Ti 3d states are marked and they are mainly composed of d_{x^2−y^2} and d_{xy} states.

FIG. 8: Charge and spin density maps for the superlattice with AlO_2/TiO_2 interfaces and 2 vacancies. The effect of relaxation is too small to be seen in this scale. Notice that only one of the interfaces is magnetic.

B. LaO/TiO_2 heterointerface

To study this heterointerface we use the supercell depicted in Fig. 5(b) and perform oxygen vacancies to simulate experimental growth conditions. It is more favorable to perform them in the TiO_2 layer compared to the LaO face. Introducing vacancies in this case is overall less favourable compared to the other interface and magnetic solutions are only found with many oxygen vacancies present, as shown in Table 1. As in this case both interfaces of the superlattice are identical, the magnetic moment per Ti atom at the surface is considerably smaller than in the previous interface. In Fig. 2(d) we can see that hybridization of La 4f with Ti 3d electrons is large, probably exaggerated by the LDA approximation, as was mentioned in Ref. 30. Comparing the valence electron charge inside the muffin-tin spheres for Ti with those of their counterparts in bulk, we corroborate a mixed valency state for the Ti atoms at the interface without vacancies while in the previous superlattice it was due to the vacancies.

Atomic relaxation in this interface is considerably smaller than in the previous one.

C. Cohesive energies

As a very first approximation one could estimate the cohesive energies of the systems in their relaxed structures by subtracting the energy of the conforming atoms from the total energy of the system. By doing so we obtain that a 5 layer slab of LAO prefers the termination AlO_2 over LaO. The cohesive energy of a superlattice with AlO_2/TiO_2 interfaces is also larger than that with LaO/TiO_2 interfaces.

A better approximation to the cohesive energy of a superlattice, given in Table 1, is to subtract from its total energy the energy of the relaxed slabs of TiO_2 and LAO that compose it. This gives a more interesting result: 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. It is important to note that the energy difference between cases with one and two vacancies is order of magnitude smaller compared to the cases with no vacancies. Therefore, with our results we can draw qualitative conclusions comparing cases either with or without vacancies but not referring to the concentration of vacancies.
The table below shows the cohesive energies and total magnetic moments per unit cell for the two types of superlattices considered, with or without vacancies (vac). The effect of lattice relaxation is indicated by the arrows for the magnetic moments. The number of vacancies is the number of missing oxygen atoms from the anatase side of each interface.

| case       | Ti/Al | Ti/La |
|------------|-------|-------|
|            | E (eV) | μ (μB) | E (eV) | μ (μB) |
| no vac     | 4.89  | 0.75 → 0.041 | 6.86 | 0 |
| 1 vac      | 6.65  | 0.38 → 0.26 | 6.01 | 0 |
| 2 vac      | 6.62  | 1.36 → 1.28 | 5.94 | 1.05 → 0.57 |

TABLE I: Cohesive energies and total magnetic moments per unit cell for the two types of superlattices considered, with or without vacancies (vac). The effect of lattice relaxation is indicated by the arrows for the magnetic moments. The number of vacancies is the number of missing oxygen atoms from the anatase side of each interface.

V. CONCLUSIONS

Our calculation shows that magnetism appears at the TiO\textsubscript{2} anatase surface and at the TiO\textsubscript{2}/AlO\textsubscript{2} interface when there are enough oxygen vacancies. Structural relaxation is found to be significant and produces an important effect on the superficial Ti magnetic moment, diminishing it. The experimental substrate LAO, presents large terraces in its surface but it is not clear which interface predominates. Using energetic arguments we find that TiO\textsubscript{2} deposition over both LAO layers could occur with equal probability but with different oxygen content in each case. The interface with AlO\textsubscript{2} has the largest cohesive energy when there are oxygen vacancies, while when there are no vacancies, the interface with LaO is preferred. Therefore, if the more abundant terraces have LaO termination, the magnetism observed experimentally would not be interfacial. It could be due to vacancies in the free surface of the anatase film, and the role of the substrate would be only to fix the cell size. If on the contrary the more abundant interface would be with Al, and the system is grown under low oxygen pressure, there could be a magnetic moment localized at the interface.

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