Ab initio study of magnetism at the TiO$_2$/LaAlO$_3$ interface

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Abstract

In this paper we study the possible relation between the electronic and magnetic structure of the TiO$_2$/LaAlO$_3$ interface and the unexpected magnetism found in undoped TiO$_2$ films grown on LaAlO$_3$. We concentrate on the role played by structural relaxation and interfacial oxygen vacancies.

LaAlO$_3$ has a layered structure along the (001) direction with alternating LaO and AlO$_2$ planes, with nominal charges of +1 and -1, respectively. As a consequence of that, an oxygen deficient TiO$_2$ film with anatase structure will grow preferently on the AlO$_2$ surface layer. We have therefore performed ab-initio calculations for superlattices with TiO$_2$/AlO$_2$ interfaces with interfacial oxygen vacancies. Our main results are that vacancies lead to a change in the valence state of neighbour Ti atoms but not necessarily to a magnetic solution and that the appearance of magnetism depends also on structural details, such as second neighbor positions. These results are obtained using both the LSDA and LSDA+U approximations.

Keywords: oxides, magnetism, ab-initio calculation
I. INTRODUCTION

Thin films of transition metal oxides (ZnO, TiO$_2$, HfO$_2$) were found to be ferromagnetic a few years ago, with a high Curie temperature, when doped with magnetic ions$^{1-3}$. The origin of this magnetic ordering is still debated, but meanwhile ferro-magnetism was also found doping with non magnetic ions, such as Cu$^4$, and also in undoped cases$^{5-7}$. Trying to understand this, several experimental tests were performed in different laboratories: the magnetic ion, the substrate over which the films were grown, the substrate temperature and the oxygen pressure during film growth were changed. The results are confusing, as some samples are magnetic while others are not$^8$. It now seems well established that structural defects, such as oxygen vacancies, and low dimensionality (thin films or nanoparticles) are necessary for the appearance of this type of ferromagnetism$^9$. One can understand why it is difficult to obtain reproducible results from different experimental samples, as it is hard to assess quantitatively the influence of defects or disorder in any system.

At the same time, several ab-initio calculations have been performed for these oxides in bulk$^{10-13}$, with impurities and/or defects, and different models have been proposed to produce the spin ordering. However, few calculations have discussed if surfaces or interfaces have any influence in this type of magnetism$^{14}$. LaAlO$_3$ (LAO) single crystal is an excellent substrate for epitaxial growth of many oxides, such as SrTiO$_3$, BaTiO$_3$, PbTiO$_3$ and TiO$_2$. While the surface electronic structure and atomic relaxation of those oxides$^{15}$ and the SrTiO$_3$/LAO interface$^{16,17}$ have been widely studied, the TiO$_2$/LAO interface has not. In the present paper we focus on undoped films of TiO$_2$ grown on top of a LAO substrate. This system has been found to be ferromagnetic, with a Curie temperature of about 800K$^6,7$, grown either by pulsed laser deposition or by spin coating. It is also well suited for ab-initio calculations because LAO in its cubic phase and TiO$_2$ in anatase structure, both along the (001) direction, have a very small structural misfit. In fact, thin films of TiO$_2$ using LAO as a substrate develop anatase structure, indicating epitaxial growth.

The aim of this work is to study the role played by interfacial oxygen vacancies on the magnetic properties of the interface. For this purpose, we consider a model system with a high concentration of vacancies. Under certain conditions we find a localized magnetic moment in the interfacial Ti atoms, depending not only on the presence of vacancies, but also on subtle structural details. We do not consider here the possible interaction between these localized moments.
II. THE SYSTEM

To simulate interfaces we use a super-lattice geometry, so that the system under study results periodic in 3D: ... LAO / TiO$_2$ / LAO / TiO$_2$ / ...

Figure 1 shows the unit cells of the two component materials: LAO and TiO$_2$ anatase. LAO is a layered material and along the (001) direction. The planes LaO and AlO$_2$ have nominal charges of +1 and -1, respectively. TiO$_2$ anatase is almost layered: the oxygen atoms are slightly out of the Ti planes, as indicated by the small arrows in Fig. 1. Each plane has zero nominal charge, so that the interface with LAO will restructure due to electrostatics either changing the valence of Ti from Ti$^{4+}$ to Ti$^{3+}$ or Ti$^{2+}$ or by missing oxygen atoms. In this respect, our previous preliminary work$^{14}$ showed, using total energy calculations, that it is easier to remove an oxygen atom from the anatase side of the interface than from the LAO side.

Figure 2 shows the two possible interfaces, namely the two ways of stacking to form the super-lattice, that maintain the octahedral environment of the Ti atoms. Without oxygen vacancies, our previous calculations$^{14}$ showed that neither one has a magnetic solution. With oxygen vacancies near the interface it is clear, due to electrostatics, that the AlO$_2$/TiO$_2$ interface will be preferred with respect to the LaO/TiO$_2$ one. While there is only one way of stacking in which LaO faces TiO$_2$, there are two ways with AlO$_2$ facing TiO$_2$, that we name A and B. They are shown in Fig. 3 that presents the super-lattice unit cells used in the present calculations. In order to have all interfaces in the super-lattice either of type A or type B, 7 anatase planes and 5 LAO planes are considered. If there are no oxygen vacancies, type A is clearly more stable, with lower total energy, as Al-O bonds are formed at the interface due to the off plane oxygens in the anatase structure. With oxygen vacancies, each distribution has to be studied separately.

The size of the super-cells is obtained by minimizing the total energy in each case, and the atomic positions inside the cell are allowed to relax but only in the direction of the super-lattice. The reason for this last restriction is based on our previous results, apart from making the calculation more feasible. In fact, the calculations on pure bulk rutile TiO$_2$$^{11}$ showed that oxygen vacancies can give rise to a local magnetic moment due to structural relaxation. However, this is only true for a fairly large concentration of vacancies and for a fixed cell size, which means there must be some restriction to the full structural relaxation. We could not find a similar result for bulk anatase TiO$_2$, but our assumption here is that the LAO substrate could impose such a structural restriction to the anatase film thus giving rise to magnetic solutions. Therefore, the calculations in
the present paper are performed fixing the unit cell size in the direction normal to the stacking to
that of cubic LAO (lattice constant = 3.8 Å) and relaxation is only allowed in the direction of the
super-lattice.

III. METHOD OF CALCULATION AND RESULTS

For the Density Functional Theory (DFT) calculations we have used the Wien2k code, that
is an implementation of the FPLAPW (full potential linear augmented plane waves) method, in
which the space is divided into muffin tin spheres around the atoms and an interstitial region.
Plane waves are used to describe the region outside the spheres. The number of plane waves in
the interstitial region is set by the cut-off parameter RK_{max}. In this work we use RK_{max}=7 that
corresponds to an energy cutoff of 340 eV. We consider both the local spin density approximation
LSDA and the LSDA+U one. The calculation is scalar relativistic and the atomic sphere radii
are taken to be small, so that the atomic spheres do not overlap when relaxing the structure. They
are 1.7 a.u. for Ti and Al, 1.4 a.u. for O and 2.5 a.u. for La. The number of k-points in the
Brillouin zone is 50 or 100 for the relaxation procedure and increased to 200 k-points for the
relaxed structure.

Figure 4 shows the densities of states calculated within LSDA for the component systems and
for the super-lattice. There are no magnetic solutions for any of these cases. The gap obtained
for anatase is 2.2 eV, to be compared with the experimental 3.2 eV, the gap for LAO is 4.3 eV to
be compared with the 5.6 eV experimental value. This feature of the LSDA approximation, that
gives small band gaps, can be corrected using the LSDA+U method or hybrid functionals. The
LSDA+U approach introduces an additional term based on a simple Hubbard model for electron
on-site repulsion. This removes the self-interaction error by energetically penalising partial oc-
cupation of the relevant electronic states, at the price of introducing an empirical parameter in an
ab-initio calculation.

Before studying the effect of oxygen vacancies at the interface, we start with bulk TiO_2. Figure
shows the densities of states of bulk TiO_2 anatase with one oxygen vacancy in the unit cell, for
two different concentrations and both methods of calculation, relaxing all structures separately. No
magnetic solutions are found for any of these cases. A defect state appears inside the band gap,
too close to the conduction band in the LSDA approximation, thus making the system metallic. In
the LSDA+U approximation, using U = 5 eV, the band gap increases by about 1 eV and the system
becomes a semiconductor, as the defect state is separated from the conduction band. However, using only one parameter $U$ (for the $d$ electrons of Ti) it is not possible to fit both the experimental band gap and the position of the defect state inside the gap (which is at 0.8 eV from the conduction band). It has been shown for reduced rutile $\text{TiO}_2$ surfaces that a discontinuity appears for this property as a function of $U$ at 4 eV and that a larger value is required to ensure the semiconductor character of the system as well as the correct position of the gap state\textsuperscript{23}. At this point it is important to remark that in the present work we consider a large concentration of vacancies in the interfaces, with the defect state developing into an impurity band, and therefore the exact position of the defect state is not so relevant.

Turning now to vacancies at the interface, Fig. 6 shows the densities of states for the super-cells A and B of Fig. 3 when all oxygen atoms on the anatase side of the interface have been removed, calculated with LSDA and with LSDA+$U$. This extreme case is very interesting, as the total energy of systems A and B are equal within the calculation error (1 mRy) but system B is magnetic while system A is not. The only difference between the two structures lies on the second neighbor layer of the interface, as shown by a dotted line in Fig. 3. The local distortion is similar in both cases, producing a ripple in the inter-facial $\text{AlO}_2$ layer.

The magnetic moment in case B is mostly located at the inter-facial Ti, as can be seen in Fig. 7. However, the total occupation of the $d$ orbitals in this Ti atom is very similar in cases A and B, both can be considered $\text{Ti}^{3+}$, calculated with LSDA and LSDA+$U$. In both approximations, the defect level widens to form a band that almost fills the band gap completely, due to the large number of oxygen vacancies. This wide feature inside the band gap is also found in XPS experiments\textsuperscript{24}.

IV. DISCUSSION AND CONCLUSIONS

The results shown in the previous section call our attention to the following fact: oxygen vacancies lead to a change of valence in a nearby Ti atom turning it into $\text{Ti}^{3+}$, but this does not necessarily imply that the system will have a magnetic solution. Trying to understand this unexpected result, we resort to the well known Stoner criterion. The main idea behind it is that hybridization and band splitting are competing mechanisms to lower the energy of the system. For this purpose we performed non-magnetic calculations of super-lattices A and B, in the unrelaxed structures.

The results are shown in Figures 8, 9 and 10. The stronger hybridization in case A is quite
obvious in Fig. 8: the partial density of states of orbital $d_{xz}$ of the inter-facial Ti overlaps almost completely with that corresponding to orbital $d_{z^2}$ of the subsurface Ti. In case B, the Al atom that is in the same position as the Ti subsurface atom, destroys this hybridization. It is the geometric difference in second neighbor positions which drives the system to a magnetic solution.

Another way of looking at this is by plotting the charge density, in an energy range close to the Fermi energy. This is shown in Fig. 9 and as expected it is quite different for both structures.

Fig. 10 shows that the non-magnetic total density of states at the Fermi level is larger in case B than in case A, in agreement with the presence of magnetism.

The study of this extreme example, with such a large number of inter-facial defects, shows that oxygen vacancies and consequently the presence of Ti$^{3+}$, are a necessary but not sufficient condition to obtain magnetic solutions. This result may be related to the difficulty of producing reproducible experimental results.

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Figures
FIG. 1: Unit cells of the two component materials in bulk: LAO (left) and TiO$_2$ anatase (right). The arrows on the oxygen atoms of anatase indicate the off-plane displacement with respect to the Ti plane.
FIG. 2: Schematic diagram of the two possible ways of stacking to form a super-lattice: AlO$_2$ facing TiO$_2$ (left) and LaO facing TiO$_2$ (right). The dotted lines indicate the position of the interfaces.
FIG. 3: Unit cells of the two super-lattices considered in this work. Due to the off-plane oxygens in the anatase structure and also to the differences in the second neighbor structure (shown by dotted lines) there are two types of AlO$_2$/TiO$_2$ interfaces, A (left) and B (right).
FIG. 4: Calculated densities of states of: (a) bulk TiO$_2$ anatase (b) bulk LAO, (c) Super-lattice with AlO$_2$/TiO$_2$ interfaces (relaxed structure).
FIG. 5: Calculated densities of states of bulk anatase, with two different concentrations of oxygen vacancies in the LSDA and LSDA+U approximations (U = 5 eV). The structure is relaxed separately in each case.
FIG. 6: Calculated densities of states of super-lattices A (left) and B (right) in Fig. 3 with no oxygen atoms in the Ti side of the interface, using the LSDA (top) and LSDA+U (bottom) approximations (U = 5 eV). Case A is not magnetic, so that the contributions of both spin types have been added. In case B we show spin up and spin down contributions separately, the magnetic moment of the unit cell is 2.7 $\mu_B$ and inside the muffin tin of each inter-facial Ti it is 0.65 $\mu_B$. 
FIG. 7: Charge and spin density maps for super-lattice B, near the AlO$_2$/TiO$_2$ interface with 2 oxygen vacancies. The effect of relaxation is too small to be seen in this scale, but the AlO$_2$ plane is buckled. Magnetism is mostly localized at the inter-facial Ti atom, spin isolines in the figure start at 0.01 and are spaced by 0.03. Charge isolines start at 0.1 and are spaced 0.1. The interface is indicated by a dotted horizontal line.
FIG. 8: Non-magnetic calculations for super-lattices A (left) and B (right). Top: atomic structures in the proximity of the interfaces. Bottom: local densities of states for an energy range close to the Fermi energy. Dotted line: $d_{x^2-y^2}$ of the inter-facial Ti, broken line: $d_{xz}$ of the inter-facial Ti and full line: $d_{z^2}$ of the subsurface Ti atom. Interface A shows a much stronger hybridization (bonding) between orbitals of inter-facial and subsurface Ti atoms.
FIG. 9: Charge densities at interfaces A (left) and B (right) in the energy range $E_f - 0.5\text{eV} < E < E_f$, plotted for $yz$-plane of Fig. 8. The isolines start at 0.04 and are spaced by 0.02.
FIG. 10: Calculated non magnetic total densities of states for super-lattices A (full line) and B (dotted line). At the Fermi level their values are 7.2 for case A and 11.5 for case B, indicating that case B has a larger probability of being magnetic.