Tuning the insulator-metal transition in oxide interfaces: an ab initio study exploring the role of oxygen vacancies and cation interdiffusion
--Manuscript Draft--

Manuscript Number:	pssb.201451050R2
Full Title:	Tuning the insulator-metal transition in oxide interfaces: an ab initio study exploring the role of oxygen vacancies and cation interdiffusion
Article Type:	Original Paper
Section/Category:	
Keywords:	DFT calculations; oxide heterostructures; Metal-insulator transition; oxygen vacancies
Corresponding Author:	Valeria Ferrari, PhD CONICET, Argentina San Martin, Buenos Aires ARGENTINA
Additional Information:	
Question	Response
Please submit a plain text version of your cover letter here. Please note, if you are submitting a revision of your manuscript, there is an opportunity for you to provide your responses to the reviewers later; please do not add them to the cover letter.	Dear Editor, We are resubmitting here our paper entitled "Tuning the insulator-metal transition in oxide interfaces: an ab initio study exploring the role of oxygen vacancies and cation interdiffusion". We have made some changes in the text to clarify the points raised by Reviewer #3 and have responded to all his/her comments. We hope that you will find our manuscript in the present form acceptable for publication in Physica Status Solidi. Yours sincerely, Valeria Ferrari
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	CONICET, Argentina
Corresponding Author's Secondary Institution:	
First Author:	Valeria Ferrari, PhD
First Author Secondary Information:	
Order of Authors:	Valeria Ferrari, PhD
	Mariana Weissmann
Order of Authors Secondary Information:	
Abstract:	We investigate the structural, electronic and magnetic properties of a particular interface in the oxide heterostructures LaAlO3/SrTiO3 (LAO/STO) and TiO2-anatase/LaAlO3 (TiO2/LAO), namely the interface of AlO2 facing TiO2 which is the energetically preferred one in the presence of interfacial oxygen vacancies. The optimum stacking for the ground state is different for each heterostructure with the interfacial Ti atoms being located either at hollow or bridge sites facing the AlO2 surface layer. This structural property determines the electronic character of the interface and as a consequence, in LAO/STO it is metallic while in TiO2/LAO it can be semiconducting and magnetic for a large concentration of vacancies. In addition, we

find that cation interdiffusion at this interface is an energetically favored defect in both heterostructures with interfacial vacancies. Its main effect is to increase the size of the band gap in the
semiconducting case and to open up a gap in the metallic one, thus allowing for a tuning of a metal to insulator transition.

Tuning the insulator-metal transition in oxide interfaces: an ab initio study exploring the role of oxygen vacancies and cation interdiffusion

V. Ferrari[*,1,2]**, M. Weissmann**[1,2]**,**

[1] Departamento de Física de la Materia Condensada, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Gral. Paz 1499, 1650 San Martín, Buenos Aires, Argentina
[2] Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina.

* Corresponding author: e-mail ferrari@tandar.cnea.gov.ar, Phone: +54-11-67727097, Fax: +54-11-67727121

We investigate the structural, electronic and magnetic properties of a particular interface in the oxide heterostructures $LaAlO_3$/$SrTiO_3$ (LAO/STO) and TiO_2-anatase/$LaAlO_3$ (TiO_2/LAO), namely the interface of AlO_2 facing TiO_2 which is the energetically preferred one in the presence of interfacial oxygen vacancies. The optimum stacking for the ground state is different for each heterostructure with the interfacial Ti atoms being located either at hollow or bridge sites facing the AlO_2 surface layer. This structural property determines the electronic character of the interface and as a consequence, in LAO/STO it is metallic while in TiO_2/LAO it can be semiconducting and magnetic for a large concentration of vacancies. In addition, we find that cation interdiffusion at this interface is an energetically favored defect in both heterostructures with interfacial vacancies. Its main effect is to increase the size of the band gap in the semiconducting case and to open up a gap in the metallic one, thus allowing for a tuning of a metal to insulator transition.

1 Introduction Oxide heterostructures are currently attracting widespread attention due to the wealth of phenomena observed at their interfaces [1]. These findings have been primarily driven by the sophistication in experimental techniques that made possible the fabrication of materials at an atomic precision level. Systematic piling of oxide monolayers allow the formation of a diversity of heterostructures. In particular, thin films of LAO grown over STO in the (001) direction display a variety of physical phenomena depending mostly on the type of interface: two dimensional conductivity, magnetism and superconductivity[2,3]. Metallicity and magnetism were indeed

unexpected properties out of the combination of two materials that are band insulators and nonmagnetic in bulk, but the profusion of the observed phenomena might well reside in the interplay of the electronic, spin and structural degrees of freedom that usually takes place in transition metal oxides (TMO) [1]. The path to understand these observations is not smooth because defects such as cationic or oxygen vacancies are usually present in TMO crystals and they appear as variables that cannot be easily controlled. Many experimental and theoretical studies took up this challenge [4–7,3,8–10] and it is the blend of all these fundamental research issues what makes oxide heterostructures physics so rich and exciting, anticipating the possibility of novel devices in the promising field of oxide electronics [10].

LAO/STO heterostructures display a two dimensional electron gas [11,12] only when the interface side of STO involves a TiO_2 layer, but the origin of this metallic state is yet under debate. Several scenarios have been drawn to explain this phenomenon but three of them have emerged as the main mechanisms invoked and the starting point is the fact that these heterostructures have interfaces between a polar material, LAO, with a non-polar one, STO. The polar character of LAO induces an electric dipole that increases with the thickness of the LAO slab and this diverging dipole has to be overcome by nature somehow. One scenario proposes that, in the case of an abrupt and sharp epitaxial interface, there should be a band bending in successive layers leading to a charge transfer from the surface of the LAO slab towards the Ti atoms at the interface and this electronic reconstruction mechanism could eliminate the dipole. This is usually called the "polar catastrophe" mechanism and assumes that the perovskite structure is maintained at the interface, so that a TiO_2 layer faces a LaO layer. Another scenario focuses on oxygen vacancies as a possible source for an extra charge to compensate the diverging electric dipole. This idea is usually advocated to explain the evolution of the resistance with temperature when changing the growth oxygen pressure in LAO/STO samples [13,14]. However, the concentration and location of oxygen vacancies is not easily obtained from experiments. Some authors propose that if the interface has a LaO layer facing a TiO_2 layer -as in the previous case-, vacancies are formed at the LAO surface [15–19]. Other authors assume [13,20] instead that LAO is grown over a highly oxygen deficient TiO_2-terminated STO substrate [21]. This assumption makes perfect sense from the electrostatics point of view if the interface is AlO_2-TiO_2. The vacancies in the TiO_2 plane render it positively charged and thus prone to face the negatively charged AlO_2 plane. It is on this AlO_2-TiO_2 interface with oxygen vacancies that we focus our work in this article. An experiment supporting the idea that oxygen vacancies are required for conduction shows that a metallic as-grown sample is opaque while the oxygen-rich post-annealed sample is transparent as insulating STO [22]. A third scenario also questions the existence of a perfect interface and proposes instead

an atomic reconstruction mechanism such as cation intermixing at the interface which has already been observed by spectroscopy [23] and diffraction [24,25] experiments. In fact, first principles calculations in LAO/STO show that exchanging Sr by La and Ti by Al for the LaO-TiO_2 interface result in more stable interface structures than the abrupt model [23]. In this work we explore whether this intermixing is also viable in the TiO_2-AlO_2 interface when oxygen vacancies are present.

One of the component materials of LAO/STO, namely LAO, is also typically used for epitaxial growth of high-quality TiO_2-anatase thin films due to their extremely small lattice mismatch [26] making the TiO_2/LAO heterostructures readily available as well. TiO_2 in both its ground state rutile structure and in the anatase one, is a currently used oxide with diverse applications such as pigments, cosmetics, catalysis, solar cells, gas sensors, photovoltaics and it has been recently proposed as a promising oxide for spintronics applications [27]. As STO, TiO_2 is a formally $3d^0$ transparent wide-gap insulator and when facing LAO, a $4f^0$ insulator, unexpected physical properties such as magnetism and 2D conductivity appear [28]. This is indeed puzzling as these two properties are thought to be related to the $3d$ level population of the Ti ions. TiO_2/LAO heterostructures could then also display the richness of physical phenomena available in LAO/STO though it has not yet been explored thoroughly. One of the issues that received widespread attention, and subject of our previous work [29,30], is the appearance of ferromagnetism in TiO_2 films grown over a LAO substrate, both upon doping the films with magnetic impurities [31] or even for pure samples [32]. A consensus on this subject has not been reached yet and, as in the case of the mentioned LAO/STO heterostructure, the sample quality and the control of defects have made the road bumpy. Interestingly, the ingredients to understand the magnetic properties in TiO_2/LAO are similar to the ones proposed to explain the metallicity in LAO/STO heterostructures, namely oxygen vacancies, intermixing, defects and charge transfer mechanisms. This coincidence might well be related to the common features appearing in both heterostructures and it is worth wondering whether these two phenomena are inter-playing somehow in the physics of these heterostructures and that in a sample, possibly more than one of the conjectured scenarios might be taking place at the same time.

The two above mentioned heterostructures have in common two interfaces, namely TiO_2-LaO and TiO_2-AlO_2, although the 3D crystallographic structures involved are different. Anatase is a more open structure than STO and the oxygen atoms are slightly off-plane with regard to the Ti atoms. We found that in both heterostructures, the TiO_2-LaO interface is the lowest in energy when there are no defects but if the interface has oxygen vacancies, the electrostatic force increases the cohesion and then the TiO_2-AlO_2 interface is the preferred one. In this paper we concentrate our study on the LAO/STO and TiO_2/LAO
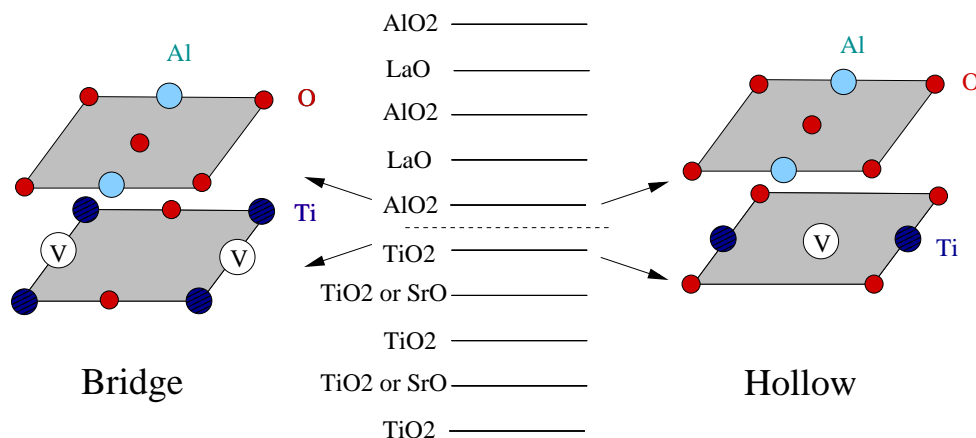
Figure 1 (color on-line) Schematic representation of the layers considered in the slab calculation to study the AlO_2-TiO_2 interface with oxygen vacancies. Both heterostructures, TiO_2/LAO and LAO/STO, have in common the LAO side (composed of AlO_2 and LaO layers). STO has SrO layers in between the TiO_2 layers, while anatase is constituted by TiO_2 layers only. Therefore, the layers labeled in the picture as "TiO_2 or SrO" stand for TiO_2/LAO or LAO/STO, respectively. Light blue (light grey) balls denote Al atoms, blue (black) balls represent Ti atoms and small red (dark) balls are the oxygen atoms. White circles with a "v" letter inside stand for the location of the oxygen vacancies. The bridge interface structure is pictured on the left and the hollow configuration, on the right.

heterostructures with oxygen vacancies and explore the role of cationic intermixing in the TiO_2-AlO_2 interface.

2 Calculational details Density Functional Theory (DFT) calculations are performed using the WIEN2k code [33] which is an implementation of the full potential linear augmented plane waves (FP-LAPW) method. The calculations are scalar relativistic and the parameters used are listed in Ref.[34].

We consider both the local density approximation (LDA) as well as LDA+U adding a local Coulomb interaction term $U = 5.44$ eV on the Ti d orbitals. The results for energy differences are qualitatively the same for LDA and LDA+U but this is not the case for the densities of states (DOS). We present only results with the LDA+U method, that gives a more accurate bandgap and location of the impurity states. The U value is chosen so as to reproduce the transition temperature of the Magneli phases in Ti_4O_7 [35].

The heterostructures are modeled by a 3D unit cell composed of slabs with 5 layers of each oxide containing the TiO_2-AlO_2 interface and a vacuum space of 10-layers size so that the constituting slabs do not interact with each other. In all the calculations, the in-plane lattice parameter is fixed to a =3.8 Å. This is the experimental lattice constant of LAO(001) and we therefore neglect the small mismatch with STO(001) (less than 3%) and the even smaller misfit with TiO_2-anatase (001). In these calculations, as we are interested in interfacial properties, we consider the substrate and the epitaxial film, on equal footing. We use an

odd number of layers of each material, to avoid the increasing dipole moment that appears when an even number of layers are successively added. Although 5 layers are certainly not enough to calculate a surface energy, we show later that 5 layers of each material is enough to compute the energy difference among several structures and the work required to separate the interfaces.

There are different ways of stacking TiO_2 facing AlO_2 as previously reported [26, 36]. In this work we only consider the two lowest energy structures: a configuration with the Ti atoms at the center of the four Al atoms, that we call "hollow" and another one with the Ti atoms bridging the Al atoms, that we call "bridge" (see Fig. 1). To study the effect of interfacial oxygen vacancy concentration, we performed simulations for two different unit cells. On the one hand, the 1x1 surface unit cell shown in Fig. 1, that renders 50% vacancies at the interface. On the other hand, a $\sqrt{2}$x$\sqrt{2}$ surface cell with one vacancy per unit cell and therefore 25% interfacial vacancies. Oxygen vacancies generate a surplus charge that in the first case is not compensated by the polar character of the $LaAlO_3$ layers, but it is neutralized in the latter case. All the atomic structures are allowed to relax till the forces on each atom are less than 0.05 eV/Å.

3 Results

3.1 Effect of oxygen vacancies at the interfacial TiO_2 layer The stability of the different interfaces in LAO/STO without oxygen vacancies, has been investigated by Albina *et al.* [37] using ab initio calcu-

lations. They considered not only interfaces with regular perovskite stacking (SrO-AlO$_2$ and LaO-TiO$_2$) but also interfaces with planar stacking-fault-like defects of Ruddlesden-Popper-type (SrO-LaO) and Magneli-type (TiO$_2$-AlO$_2$). They found that the regular stacking interfaces were more stable than the interfaces containing planar defects. However, our present study includes oxygen vacancies and in this case, the most stable interface is TiO$_2$-AlO$_2$, as it was previously found in TiO$_2$/LAO[29]. The reason for this change in stability lies in the fact that in this interface, the electrostatic energy provided by oxygen vacancies overcomes the extra energy required for producing a Magneli-type defect, thus making the TiO$_2$-AlO$_2$ interface the preferred one in the presence of vacancies.

Heterostructure	LaO-TiO$_2$	AlO$_2$-TiO$_2$		Reference
		H	B	
LAO/STO	3.62	-	2.21	Ref.[37]
	3.35	0.41	2.34	This work
TiO$_2$/LAO	4.03	2.16	1.76	Ref.[26]
	3.80	-	2.71	Ref.[29]
	3.29	0.21	1.06	This work
LAO/STO with vacancies	3.03	1.68	4.09	This work
TiO$_2$/LAO with vacancies	2.52	3.12	2.94	Ref.[26]
	3.33	-	3.69	Ref.[29]
	2.43	4.64	4.12	This work

Table 1 Work required to separate the interfaces (in J/m^2) for both heterostructures without vacancies and with 50% of oxygen vacancies at the interface. H stands for Hollow and B for bridge structures.

Using ab initio calculations, we obtain a first approximation of the stability of the different interfaces by evaluating the energy required to separate each heterostructure into two independent slabs. To evaluate this work of separation, we take into account the relaxed structures because atomic relaxation might be significant due to defects at the interfaces. The results of the present article along with previously reported works are summarized in Table 1. From this Table we can draw the following conclusions: without vacancies, the most stable interface is LaO-TiO$_2$ with a cohesive energy of around 3.3 J/m^2. When oxygen vacancies are formed at the interface and in particular for a 50% concentration, the AlO$_2$-TiO$_2$ interface has a cohesive energy of around 4 J/m^2. The numerical differences observed in Table 1 arise because other authors' calculations [37,26] have been performed under different conditions such as supercell or slab calculations, LDA or LDA+U, charged or neutral cells, etc. However, it is remarkable that the separation energy seems to be a qualitatively robust result so that the conclusions regarding the preferred interface remain unchanged. To the best of our knowledge, the stability of LAO/STO with oxygen vacancies has not been
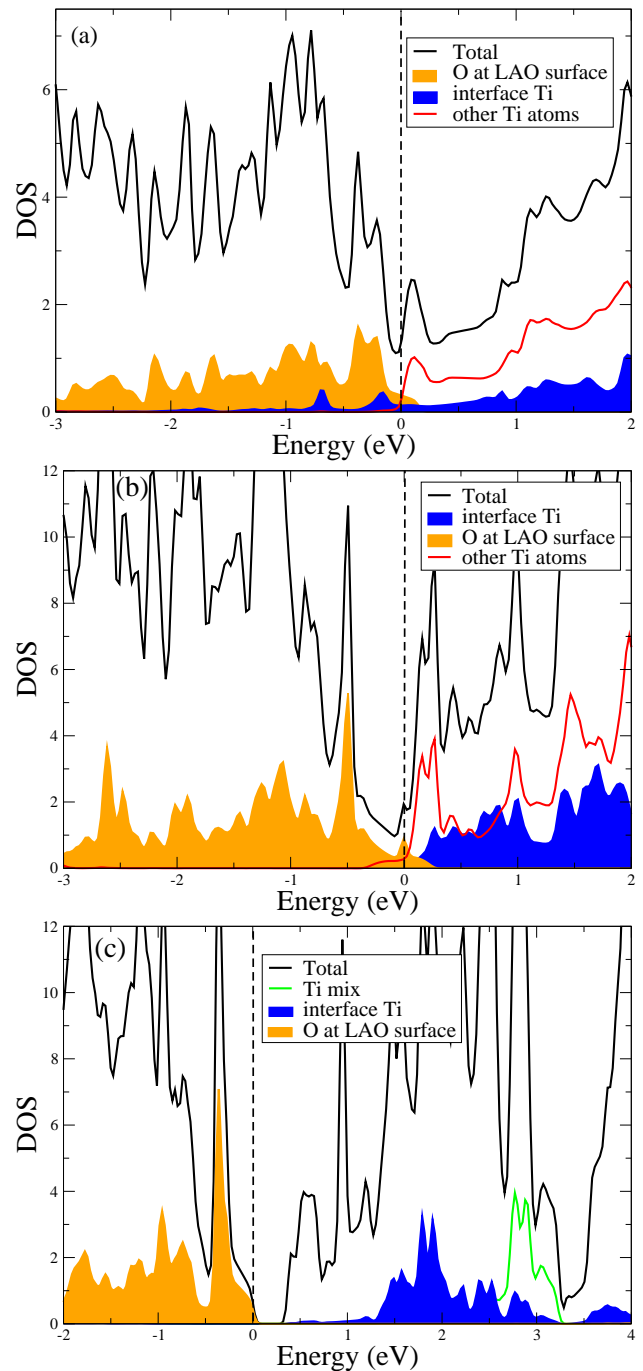

Figure 2 (color on-line) DOS for the LAO/STO slab with bridge structure.(a) 50 % of oxygen vacancies. (b) 25 % of oxygen vacancies. (c) considering intermixing of Al and Ti at the interface for 25 % of oxygen vacancies.

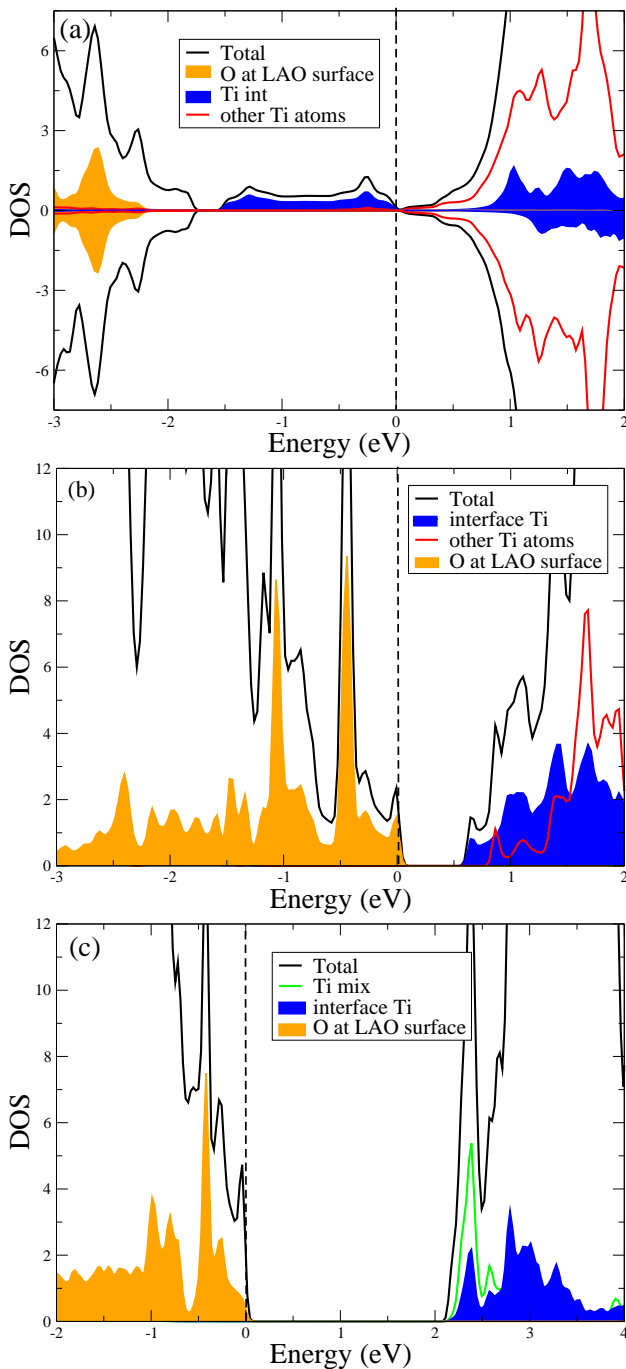theoretically explored before and our results show that the preferred interface in the presence of interfacial vacancies is AlO$_2$-TiO$_2$.
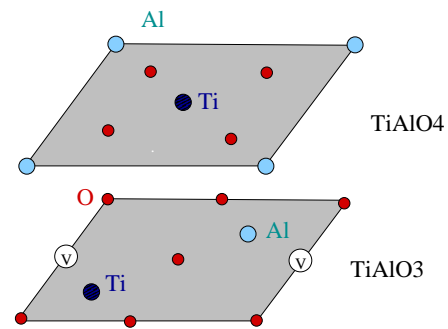
Figure 4 (color on-line) Layers involved at the interface of the heterostructures when considering intermixing of Al and Ti ions in both TiO_2/LAO and LAO/STO, in the presence of 25% of oxygen vacancies. The color-coding of the different atoms is the same of Fig. 1.

Figure 3 (color on-line) DOS for the TiO_2/LAO slab with hollow structure. (a) 50 % of oxygen vacancies. (b) 25 % of oxygen vacancies. (c) considering intermixing of Al and Ti at the interface for 25 % of oxygen vacancies. Top and bottom panel in (a) represent the majority and minority spin contributions, respectively as in this case the system is magnetic.

The TiO_2/LAO heterostructure presents only two types of interfaces, namely TiO_2-AlO_2 and LaO-TiO_2. In sim-

ilarity with the LAO/STO heterostructure, the LaO-TiO_2 interface is more stable in the absence of oxygen vacancies, but with oxygen vacancies again the electrostatic energy makes up for the extra energy required to produce the Magneli-type defect[29] as shown in Table 1. We have calculated hollow and bridge stackings in both heterostructures and it turns out that in LAO/STO, the preferred one is the bridge position while in TiO_2/LAO, the lowest energy configuration is the hollow one [26]. In the following we show that this stacking difference brings about dramatic changes in the conducting properties.

Comparing the DOS for the hollow or bridge stacking in both heterostructures, we found that the electronic properties are strongly dependent on the piling structure. In other words, different heterostructures with the same piling present the same electronic properties. In Fig. 2 and Fig. 3, we show the DOS for the ground state piling for each heterostructure, namely bridge for LAO/STO and hollow for TiO_2/LAO. In bridge structures, there is no gap and the contributions at the Fermi level come from interfacial Ti states as well as from oxygen levels at the LAO surface as it is shown in the projected DOS of Fig. 2(a) and (b). Therefore, as for LAO/STO the most stable structure is bridge, it is always conducting with or without oxygen vacancies. As a consequence, there is conduction at the surface of LAO as well as at the interface, in a similar fashion to the polar catastrophe scenario that occurs at the LaO-TiO_2 interface. However, in this latter case, the 2D electronic gas appears for a LAO thickness of more than 4 unit cells, while in the present interface it is already present for a smaller LAO thickness.

The TiO_2/LAO heterostructure, being in the hollow structure, is either semiconducting and magnetic [36] for a 50% of oxygen vacancies (Fig. 3(a)) or it opens a gap for a 25% of oxygen vacancies (Fig. 3(b)). It is important to note that these effects arise due to the presence of oxygen vacancies. The fact that, decreasing the number of vacan-
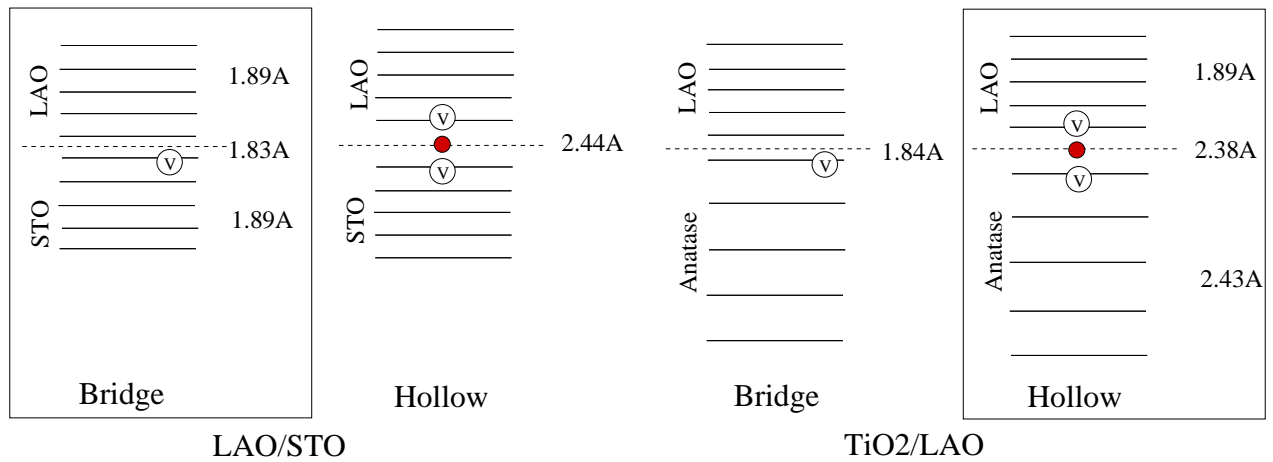
Figure 5 (color on-line) Schematic picture of the effect produced by relaxation at the interface layers of the heterostructures for either bridge or hollow arrangements. The ground state structure in each case is marked by a box. There is an important buckling at the interface but we only show the minimum distance between atoms at the interface and the bulk interlayer distances. In hollow structures the oxygen atom (represented by a red (dark) circle) lying just atop the vacancy site relaxes towards the center of the interface leading in practice to two vacancy sites.

cies the system becomes insulator is in agreement with the observed metallic to insulating transition due to oxygen vacancies found in LAO/STO heterostructures [22].

We have performed test calculations with a larger number of layers of the component materials and the main DOS features remain, although there are small changes in the Fermi level position and/or the size of the gap.

3.2 Effect of cation intermixing at the interface
Cation intermixing at the interface is another candidate put forward for explaining the mechanism of conductivity in LAO/STO [24, 23] and the stoichiometry of LAO was found to be determinant in the formation of 2D electronic states[38]. To further explore the role of imperfect interfaces, in this section, we discuss the effect of intermixing in the presence of oxygen vacancies.

An important antecedent in this respect is a DFT calculation for bulk TiO_2-anatase, considering Al doping. It shows that, in the presence of oxygen vacancies, the introduction of Al ions lowers the total energy [39]. This fact suggests the existence of an interfacial defect exchanging Ti and Al atoms in the interface under study when there are oxygen vacancies. With this motivation, we study the effects on the electronic properties due to Al-Ti exchange in both LAO/STO and TiO_2/LAO heterostructures. For the calculations we take a $\sqrt{2}x\sqrt{2}$ cell and exchange one Ti atom by one Al atom at the interface, as shown in Fig. 4. As a consequence, we have an interface composed by a layer of $TiAlO_4$ facing a $TiAlO_3$ one, when considering oxygen vacancies.

From the energetics point of view, we found that this intermixing process lowers the total energy in both heterostructures. In the LAO/STO case, the gain in energy is 1.8 eV while in TiO_2/LAO, it is 1.2 eV. Therefore, this kind of intermixing defect at the interface, would be quite plausible in the experiments.

Regarding the stability of the heterostructures, we found that the piling structure that was stable for each heterostructure before intermixing, either hollow or bridge, is not affected by this exchange of atoms. However, the electronic properties do change as can be seen in Fig. 2 (c) and Fig. 3 (c). The effect of intermixing is that the LAO/STO heterostructure that was conducting turns insulating due to a gap appearing at the Fermi level and the TiO_2/LAO structure, which was insulating, increases the size of its gap. Therefore, intermixing of Ti and Al atoms might be one of the experimental causes hindering the presence of a 2D electron gas at the interface. However, one should note that our conclusions hold for this neutral system but if the proportion of mixing and vacancies is different, this scenario might change.

3.3 Discussion A question remains and it is why these two heterostructures having almost identical interfaces, have so different electronic properties? One of the clues lies in the structure, with bridge arrangements being conducting while hollow ones are insulating, but the ultimate question is why the ground state in LAO/STO is bridge while in TiO_2/LAO it is hollow? A key point is to look at the relaxed interlayer distance at the interface and compare it with the bulk structures of the oxides

composing the heterostructure. In bridge stackings, this distance is primarily determined by the bond formed by an interfacial Ti atom (either at STO or TiO$_2$-anatase) with the oxygen atom from the LAO side lying just atop (see Fig. 1), d$_{TiO}$=1.8 Å. In hollow structures, this interlayer distance is determined by the distance between the oxygen atoms facing each other in their respective interface layers (see Fig. 1) which is much greater, d$_{OO}$= 2.4 Å. The bulk interplanar distances of the composing heterostructures are d$_{STO}$=d$_{LAO}$ =1.89Å and d$_{anatase}$=2.43 Å (see Fig. 5). That is, the perovskite structures STO and LAO are both more compact than anatase and prefer the bridge arrangement, while the heterostructure involving anatase, prefers the hollow structure, thus changing completely the electronic properties. It is important to note that this is a feature due to the oxygen vacancies because without them, both heterostructures have the bridge stacking. When oxygen vacancies are present, the oxygen just atop a vacancy in the hollow structure, relaxes towards the anatase providing the Ti atoms with extra ligands to oxygen atoms. At the same time, the oxygen atoms of both sides of the interface repel each other, providing an anatase-like interlayer distance at the interface. In bridge structures, the interfacial oxygen atoms relax towards the Ti and Al atoms at the interface thus providing extra bonds and turning the system metallic.

4 Conclusions We have performed an ab initio study of two oxide heterostructures, namely LAO/STO and TiO$_2$/LAO. We have focused on the effect of oxygen vacancies with or without cationic intermixing at the TiO$_2$-AlO$_2$ interface.

We found that this interface can be either insulating or metallic, depending on the preferred stacking for each heterostructure. In particular, the ground state in LAO/STO with oxygen vacancies at the interface, presents a stacking where interfacial Ti atoms face bridge sites of the AlO$_2$ surface plane while in the TiO$_2$/LAO case, they face hollow sites. The stacking is indeed the property that determines the electronic character of the interface with the hollow structure being insulating and the bridge one being metallic. In addition, ion interdiffusion along with oxygen vacancies is a defect that is energetically favorable and it allows for a tuning of a metal to insulator transition as its main effect is to increase the size of the band gap in the TiO$_2$/LAO insulating case and to open up a gap in the LAO/STO metallic one.

References

[1] P. Zubko, S. Gariglio, M. Gabay, P. Ghosez, and J. M. Triscone, Annu. Rev. Condens.Matter Phys. **2**(141-65) (2011).

[2] S. A. Chambers, Surface Science **605**, 1133–1140 (2011).

[3] J. A. Bert, B. Kalisky, C. Bell, M. Kim, Y. Hikita, H. Y. Hwang, and K. A. Moler, Nature Physics **7**, 767 (2011).

[4] N. C. Bristowe, E. Artacho, and P. B. Littlewood, Phys. Rev. B **80**, 045425 (2009).

[5] M. Salluzzo, J. C. Cezar, N. B. Brookes, V. Bisogni, G. M. De Luca, C. Richter, S. Thiel, J. Mannhart, M. Huijben, A. Brinkman, G. Rijnders, and G. Ghiringhelli, Phys. Rev. Lett. **102**, 166804 (2009).

[6] R. Pentcheva and W. E. Pickett, J. Phys.: Condens. Matter **22**, 043001 (2010).

[7] K. J. Zhou, M. Radovic, J. Schlappa, V. Strocov, R. Frison, J. Mesot, L. Patthey, and T. Schmitt, Phys. Rev. B **83**, 201402 (2011).

[8] C. Cantoni, J. Gazquez, F. Miletto Granozio, M. P. Oxley, M. Varela, A. R. Lupini, S. J. Pennycook, C. Aruta, U. Scotti di Uccio, P. Perna, and D. Maccariello, Advanced Materials **24**, 3952 (2012).

[9] M. L. Reinle-Schmitt, C. Cancellieri, D. Li, D. Fontaine, M. Medarde, E. Pomjakushina, C. W. Schneider, S. Gariglio, P. Ghosez, J. Triscone, and P. R. Willmott, Nature Communications **3**, 932 (2012).

[10] J. Chakhalian, A. J. Millis, and J. Rondinelli, Nature Materials **11**, 92 (2012).

[11] A. Ohtomo and H. Y. Hwang, Nature **427**, 423–426 (2004).

[12] M. Bastelic, J. L. Maurice, C. Carretero, G. Herranz, O. Copie, M. Bibes, E. Jacquet, K. Bouzehouana, S. Fusil, and A. Barthelemy, Nature Materials (2008).

[13] G. Herranz, M. Basletic, M. Bibes, C. Carretero, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzic, J. M. Broto, A. Barthelemy, and A. Fert, Phys. Rev. Lett. **98**, 216803 (2007).

[14] W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank, and M. R. Beasley, Phys. Rev. Lett. **98**, 196802 (2007).

[15] C. Cen *et al.*, Nature Materials **7**, 298 (2008).

[16] N. C. Bristowe, P. B. Littlewood, and E. Artacho, Phys. Rev. B **83**, 205405 (2011).

[17] Y. Li *et al.*, Phys. Rev. B **84**, 245307 (2011).

[18] N. Pavlenko, T. Kopp, E. Y. Tsymbal, J. Mannhart, and G. A. Sawatzky, Phys. Rev. B **86**, 064431 (2012).

[19] G. Berner *et al.*, Phys. Rev. Lett. **110**, 247601 (2013).

[20] N. Pavlenko, T. Kopp, E. Y. Tsymbal, G. A. Sawatzky, and J. Mannhart, Phys. Rev. B **85**, 020407(R) (2012).

[21] A. F. Santander-Syro *et al.*, Nature **469**, 189 (2011).

[22] S. S. A. Seo, Z. Marton, W. S. Choi, G. W. J. Hassink, D. H. A. Blank, H. Y. Hwang, T. W. Noh, T. Egami, and H. N. Lee, Appl. Phys. Lett.(95), 082107 (2009).

[23] L. Qiao, T. C. Droubay, V. Shutthanandan, Z. Zhu, P. V. Sushko, and S. A. Chambers, J. Phys.: Condens. Matter **22**, 312201 (2010).

[24] P. R. Willmott, S. A. Pauli, R. Herger, C. M. Schlepütz, D. Martoccia, B. D. Patterson, B. Delley, R. Clarke, D. Kumah, C. Cionca, and Y. Yacoby, Phys. Rev. Lett. **99**, 155502 (2007).

[25] Z. Q. Liu, C. J. Li, W. M. Lü, X. H. Huang, Z. Huang, S. W. Zeng, X. P. Qiu, L. S. Huang, A. Annadi, J. S. Chen, J. M. D. Coey, T. Venkatesan, and Ariando, Phys. Rev. X **3**, 021010 (2013).

[26] Z. Wang, W. Zeng, L. Gu, M. Saito, S. Tsukimoto, and Y. Ikuhara, Journal of Applied Physics(108), 113701 (2010).

[27] U. Diebold, Surf. Sc. Reports **48**, 53 (2003).

[28] K. S. Takahashi and H. Y. Hwang, Appl. Phys. Lett **93**, 082112 (2008).

[29] M. Weissmann and V. Ferrari, J. of Phys: Conf. Ser. **167**, 012060 (2009).

[30] M. Weissmann, V. Ferrari, and A. Saul, J. Materials Science **45**, 4945 (2010).

[31] J. M. D. Coey, P. Stamenov, R. D. Gunning, M. Venkatesan, and K. Paul, New Journal of Physics **12**, 053025 (2010).

[32] N. H. Hong, J. Sakai, N. Poirot, and V. Brizé, Phys. Rev. B **73**, 132404 (2006).

[33] P. Blaha, K. Schwarz, G. Madsen, D. Kvaniscka, and J. Luitz, WIEN2k: An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties, TU Wien, Austria, 2001, http://www.wien2k.at.

[34] For the FP-LAPW calculations, we have used the following parameters: Atomic sphere radii of 1.7 Bohr for Ti and Al; 1.4 Bohr for O; 2.5 Bohr for La and Sr. The convergence control parameter RKmax was chosen to be 6, which corresponds to an energy cutoff of 250 eV. A k-point mesh of 10x10x1 in the irreducible Brillouin zone was used.

[35] M. Weissmann and R. Weht, Phys. Rev. B **84**, 144419 (2011).

[36] M. Weissmann and V. Ferrari, Journal of Nanomaterials, 757403 (2012).

[37] J. M. Albina, M. Mrovec, B. Meyer, and C. Elsässer, Phys. Rev. B **76**, 165103 (2007).

[38] V. Vonk, J. Huijben, D. Kukuruznyak, A. Stierle, H. Hilgenkamp, A. Brinkman, and S. Harkema, Phys. Rev. B **85**, 045401 (2012).

[39] R. Shirley, M. Kraft, and O. R. Inderwildi, Phys. Rev. B **81**, 075111 (2010).