Charge localization or itineracy at LaAlO$_3$/SrTiO$_3$ interfaces: Hole polarons, oxygen vacancies, and mobile electrons

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While correlated electron behavior is to be expected at oxide interfaces (IFs) involving Mott insulators, we show how strong correlations in the oxygen 2p states may be necessary to account for observed insulating behavior at charged (001)-IFs between the band insulators LaAlO$_3$ and SrTiO$_3$. Using correlated band theory applied to the O 2p states, an insulating p-type IF is obtained only when a disproportionated, charge-, orbital-, and spin-ordered O P_π magnetic hole is formed, centered between Al^{3+} ions in the AlO$_2$ layer at the IF. As an alternative explanation, charge compensation by oxygen vacancies that accommodate the holes as charge-conjugate F centers is modeled. For the n-type IF, a charge disproportionated Ti^{4+}+Ti^{3+} layer is obtained with ferromagnetic alignment of the spins resulting from occupied d_{xy} orbitals at checkerboard arranged Ti^{3+} sites. Electron hopping on a 50% occupied Ti sublattice (a quarter-filled band) and/or lattice relaxations are discussed as origin of the measured conductivity.

I. INTRODUCTION

Nonequilibrium layer-by-layer epitaxial growth of oxide materials[1] not only has invigorated the field of nanostructure engineering but has also led to synthesis of systems with properties that differ substantially from the bulk. The novel magnetic phases realized at oxide multilayers and interfaces (IFs)[2–4] open a path toward the development of new subnanoscale spintronic devices, but also pose fundamental questions that do not arise in bulk crystals.[5] For instance, metallic conductivity was measured at band insulator-Mott insulator IFs[2,3] and theoretical investigations on the response of the Mott insulating state to conditions at the IF have been initiated.[6]

While in Mott insulators even the bulk behavior is still the subject of intensive research,[7] there are now examples of unexpected phenomena occurring in well understood, "simple" oxides when local charge compensation is violated. The questions that arise for charge-imbalanced IFs of ionic insulators have aspects in common with issues faced at polar semiconducting IFs,[8] but the way the charge is accommodated in oxides may be much more local, perhaps introducing correlated behavior. In such materials the oxygen atoms are typically not expected to be involved in the emergence of magnetism or conductivity. However, recently magnetic oxygen atoms have been predicted at polar oxide insulator surfaces,[9] around dilute cation vacancies in ionic insulators,[10] or after substitution in octuple-perovskite cuprates (e.g., Sr$_8$CaRe$_3$Cu$_4$O$_{24}$—Ref. [11]).

Intriguing results were obtained recently by Ohtomo and Hwang[4] for the IF of two common insulators SrTiO$_3$ and LaAlO$_3$. At the SrTiO$_3$/LaAlO$_3$(001) IF both the A-sublattice cations (Sr, La) and the B-sublattice metal ion (Ti, Al) change across the IF, leading to violation of local charge neutrality (based on formal charges): either the Ti^{4+} ion (in bulk SrTiO$_3$) or the Al^{3+} ion (in bulk LaAlO$_3$) has its immediate environment changed at the IF. The IFs in this system are of two types: the n-type (LaO)$^+$/(TiO$_2$)^0-IF in which one electron per La is released into the vicinity, and the p-type (AlO$_2$)$^-$/(SrO)^0-IF (cf. Fig. 1) in which there is one hole per IF Sr ion. The n-type IF is reported to be conducting, while the p-type IF is insulating[4] rather than showing the conductivity expected from unfilled IF bands.

In this paper we investigate the origin of this surprising behavior using density-functional theory considering also electronic correlations within the LDA+U approach. We focus first on the perplexing p-type IF, then explore what a similar approach reveals for the n-type IF. In Mott insulators the oxygen ions are usually considered as bystanders as far as the driving mechanism for magnetism or conductivity is concerned. At the p-type IF however, the hole carriers must lie in the oxygen 2p bands, since the only alternative is Sr or Al semicore states that are much more strongly bound. But if the holes go into the O p bands, why is this p-type IF not a
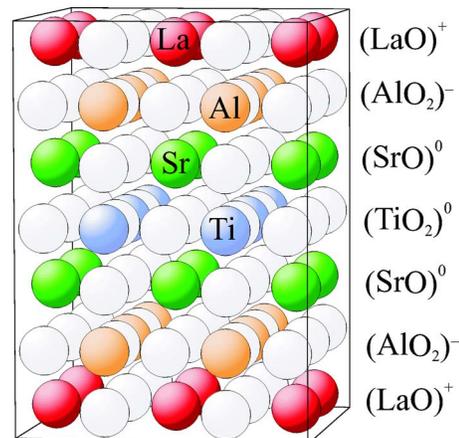

FIG. 1. (Color online) Schematic picture of the p-type (AlO$_2$)$^-$/(SrO$_2$)^0 interface, in the smallest cell with two oppositely oriented (SrO)^0-(AlO$_2$)$^-$ interfaces. White unlabeled circles denote the oxygen ions.

conductor as simple band theory would suggest, and as is observed for the n-type IF. While in Ref. 4 Ohtomo and Hwang argued that the insulating behavior at the p-type IF is intrinsic to the ideal IF, in a more recent work oxygen defects (specifically, O vacancies) were suggested to be responsible for the absence of conductivity.[12] We explore both possibilities, and also address the electronic, magnetic, and conducting behavior at the n-type IF.

II. CALCULATIONAL DETAILS

The calculations were performed using the full-potential augmented plane waves (FP-APW) method in the WIEN2k-implementation[13] and the generalized gradient approximation (GGA).[14] Electronic correlations are considered within the fully localized limit (LDA+U).[15] The minimal supercell with two p interfaces having opposing dipoles is shown in Fig. 1. To minimize the interaction between the interfaces especially for the systems containing vacancies we have used thicker slabs containing either three LaO layers or three TiO$_2$ layers for a vacancy in the AlO$_2$ or SrO layer, respectively. The lateral size of the cell is $p(2 \times 2)$ unless otherwise stated. For this cell 18 k points in the irreducible part of the Brillouin zone were used. The muffin tin (MT) radii are: $R_{La}^{MT} = 2.50$ bohr, $R_{Al}^{MT} = 2.10$ bohr, $R_{Ti}^{MT} = 1.90$ bohr, $R_O^{MT} = 1.60$ bohr. The following convergence parameters were used for the mixed APW+lo and LAPW basis set: Inside the muffin tins wave functions are expanded in spherical harmonics up to $l_{max}^{wf} = 10$ and nonspherical contributions to the electron density and potential up to $l_{max}^{pot} = 4$ are used. The energy cutoff for the plane wave representation in the interstitial is $E_{max}^{wf} = 19$ Ry for the wave functions and $E_{max}^{pot} = 196$ Ry for the potential. The Ti $3s$ and $3p$ states were treated as valence states.

III. BULK BEHAVIOR

LaAlO$_3$ (La^{3+}Al^{3+}O$_3^{2-}$), with bulk lattice parameter $a = 3.79$ Å, is a conventional band insulator with a 5.6 eV band gap between filled O $2p$ bands hybridized with Al p bands and unfilled conduction bands comprised of Al $3s$, $3p$ states and La $5d$ states. The calculated gap within the generalized gradient approximation (GGA) is 3.7 eV, shown in Fig. 2(a). The GGA gap for bulk SrTiO$_3$ (Sr^{2+}Ti^{4+}O$_3^{2-}$) in the cubic perovskite structure ($a = 3.92$ Å) is 2.0 eV, with the measured value being 3.2 eV, between filled O $2p$ bands and unfilled Ti $3d$ bands [Fig. 2(b)]. For LaAlO$_3$ a^{expt} coincides with the GGA value, for SrTiO$_3$ a^{expt} is by 0.6% smaller than a^{GGA}. The calculations for the interfaces are performed at the experimental lattice constant of SrTiO$_3$. In bulk form, SrTiO$_3$ is unstable with respect to an antiferroelectric (zone-boundary) distortion, but there has been no evidence of this distortion in recent IF studies with only a few layers of SrTiO$_3$. The lattice parameter mismatch between these oxides is about 4%, which does not impede the growth of ordered IFs between thin (multi-)layers of each material.

IV. THE p-TYPE INTERFACE

In the p-type IF a SrO layer lies next to an AlO$_2$ layer. The smallest supercell containing two oppositely oriented
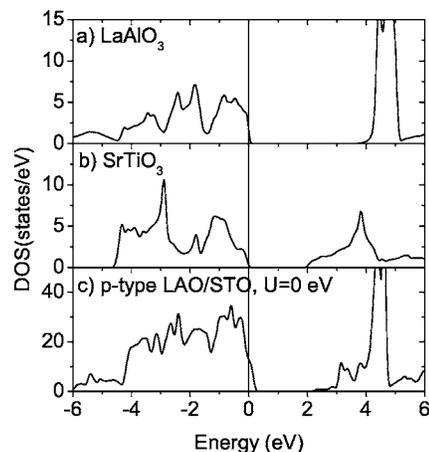

FIG. 2. LDA density of states of (a) bulk LaAlO$_3$, (b) bulk SrTiO$_3$, and (c) the p-type LaAlO$_3$-SrTiO$_3$ interface in GGA. The bulk DOS are obtained for the experimental lattice constants of the respective materials.

p-type LaAlO$_3$-SrTiO$_3$ IFs (necessary to produce oppositely directed dipoles) is shown Fig. 1. Since the two bounding LaO layers are equivalent, one finds a charge shortage of one electron, leaving one-half hole per IF cell to be confined near the IF. Here we confront the question of how a p-type IF of the type grown and characterized by Ohtomo and Hwang can be consistent with insulating behavior and explore two possible pathways: (i) the formation of a (charge-) polaron crystal at a structurally ideal IF and (ii) charge compensation due to the formation of oxygen defects. Since the valence bands (hole states) are comprised of O $2p$ orbitals, it is likely that the solution involves a multiatom, multiorbital complex satisfying charge balance, and involving some or all of: Coulomb correlations, charge disproportionation, and charge/spin/orbital ordering. The primary defect to consider is the O vacancy, which in itself would release two electrons into its vicinity. The O vacancy is a natural possibility for charge compensation and hence insulating behavior.

A. Charge disproportionation: The polaron crystal phase

The apparent atomic layer perfection of the superlattices grown by Ohtomo and Hwang[4] suggests the insulating nature is intrinsic to the ideal IF. Our approach is to probe the question: can correlation effects, which we model by the LDA+U method, produce an insulating result for the p-type IF? In the p-type IF that we address, however, the hole lies in the O $2p$ bands and there is no possibility of relevant correlation effects on the $3d^0$ Ti ion. Since the conventional LDA gives a conducting result [Fig. 2(c)], hole localization on an oxygen ion is possible only if the intra-atomic repulsion U_p is strong.

The importance of U_p on the O ion has been recognized for some time, in the high temperature superconducting cuprates,[17–20] but also in other oxides with estimates of its magnitude ranging from 3 to 8 eV. Spectroscopic data on Sr$_2$FeMoO$_6$ suggested $U_p = 3.8$ eV,[21] and for TiO$_2$ $U_p = 6$ eV was required to account for Auger spectra.[22] These "effective U" values are obtained from model Hamiltonian

studies by fitting to spectra, but they can be generally related to values appropriate for LDA+U studies. Few-band model Hamiltonian studies have used U_p=3–4 eV for cuprates[17,23,24] and U_p=5 eV for nickelates.[25] Multiband fits to constrained LDA energies produced U_p=3.5–7.5 eV[18,19] depending on the freedom allowed in the model. In a LDA+U study of NiO, MnO, and La$_2$CuO$_4$ Nekrasov *et al.* used U_p=6 eV.[20] In all these calculations though, the effect of U_d on the transition metal ion is dominating, and also the polarizability of the d electrons reduces the value of U_p. In the absence of a metal ion to help accommodate the hole in these intermediate gap semiconductors, we expect the value of U_p for the p-type IF will lie at the upper end of the 3–8 eV range and have chosen U_p=7 eV.

While the deficiency in charge must be confined to the region of the IF due to the insulating nature of LaAlO$_3$ and SrTiO$_3$, there is still a wide latitude for the choice of where and how the hole will be accommodated, and what specific collective state is preferred. After considering an assortment of possibilities, we have identified one state, involving charge+orbital+spin ordering, within which an insulating p-type IF can be understood.

There is 0.5 hole per O ion (in the SrO layer) or 0.25 per O ion (in the AlO$_2$ layer) per IF cell, so insulating behavior appears to require that the hole becomes well localized around one oxygen. Charge balance requires disproportionation on the O sublattice in a specific concentration, viz. $2O^{1.5-} \rightarrow O^{2-}+O^{1-}$ in the SrO layer, or $4O^{1.75-} \rightarrow 3O^{2-}+O^{1-}$ in the AlO$_2$ layer. To probe this possibility we apply a repulsive Coulomb interaction $U_p \approx 7$ eV on the O ions[16] (see the discussion above). Being larger than the width of the O 2p complex ($\sim$5 eV), strong correlation effects can be anticipated. Since the O 2p orbitals are (nearly) threefold degenerate, these questions of charge localization and subsequent order become further entwined with the choice of which local orbital is most favorable and if its occupation is suitable (energetically) for orbital ordering. Finally, magnetic ordering and relaxation determines the ground state.

GGA calculations show that the AlO$_2$ layer is more susceptible to hosting the hole than the SrO layer. Simple electrostatic considerations suggest holes will prefer $p\pi$ orbitals (oriented perpendicular to the nearest cation) rather than $p\sigma$ orbitals (directed toward a positive ion). To allow both a ferromagnetic (FM) and antiferromagnetic (AFM) coupling of the holes, we model the system in a $p(2\times2)$ cell containing two holes per IF cell. We have performed calculations for both FM and AFM order with a minimal supercell with two p-type IFs, which contains only one TiO$_2$ layer (shown in Fig. 1). We have checked for the FM case a larger supercell with three TiO$_2$ layers in which the IFs are better separated and find that the results we present are not influenced appreciably by the thickness of the SrTiO$_3$ slab.

FM ordering of hole spins. The LDA+U solution we obtain in the ferromagnetic case corresponds to a disproportionated magnetic hole centered on one of four O ions (denoted O$_{Al}^*$) in the AlO$_2$ layer. 60% of the charge of this somewhat extended hole state, the "P_π polaron" shown in Fig. 3, is localized on the O$_{Al}^*$ in-plane $p\pi$-orbital (p_y in the figure), and 20% of the charge on $p_x \cos\phi + p_y \sin\phi$ type orbitals ($\phi \approx \pm 25°$) on each of the four neighboring O ions in
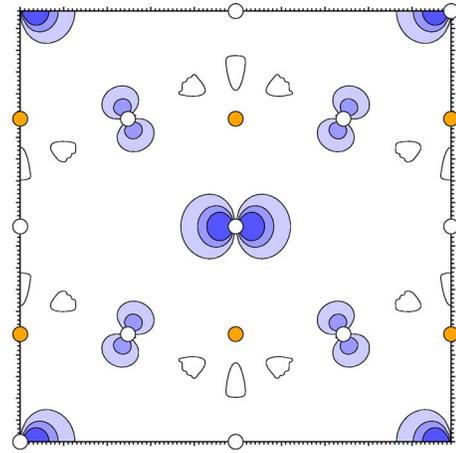

FIG. 3. (Color online) Charge density plot of the ferromagnetically coupled oxygen holes localized in the AlO$_2$ layer, illustrating the P_π hole state centered around O$_{Al}^*$ at (0.0,0.0) and (0.5,0.5). The figure contains the simulated $p(2\times2)$ supercell, the positions of O and Al atoms are marked by white and orange (gray) circles, respectively.

the Al layer (each being shared by two P_π polarons at this concentration). The four next nearest neighbors have full p states and do not contribute to the polaron. Since atomic relaxation is not required to obtain this localized hole, it represents an example of a self-trapped charge-polaron, first suggested by Landau for a lattice polaron.[26]

The moment in the O$_{Al}^*$ sphere is 0.58μ_B, that of the neighboring oxygens is 0.17μ_B. The charge-/spin-density of this *half-metallic* system is symmetry equivalent to a $(\frac{\pi}{a},\frac{\pi}{a})$ charge-/spin-density wave in the usual perovskite coordinate system and is degenerate with an equivalent state oriented at 90° and centered at a neighboring O ion. The choice of one of the two P_π-hole states breaks the square symmetry, as is evident in the density contour plot in Fig. 3.

The upper and lower Hubbard bands of this P_π-polaron lattice, pictured in Fig. 4, are split by U_p=7.0 eV as expected, with the lower band tightly bound at the bottom of the O 2p complex. (Two IFs in the cell lead to two of each type of IF band, but the very small IF-IF interaction causes no difficulty in the interpretation.) The 1.6 eV wide upper Hubbard band center lies 0.3 eV above the top of the itinerant p states. Its dispersion is described by hopping amplitudes t_1=0.20 eV, t_2=−0.025 eV. The band disperses downward toward the zone corner and overlaps a second rather flat IF band (designate it P_z), comprised mostly of O$_{Sr}$ 2p_z character (but with some O$_{Ti}$ 2p_y character). The P_z band, evident as the uppermost minority valence band in Fig. 4, mixes only weakly with the P_π band. The overlapping of the dispersive P_π-IF band with the (weakly dispersive) P_z band has three dominant effects. First, the band overlap leaves the P_π state containing only 80% of the hole, the remaining 20% being centered around Γ in the P_z band. Second, the overlap introduces majority holes and thereby polarizes the P_z states antiparallel to the P_π hole, with its exchange splitting of $\approx$0.4 eV being identifiable in Fig. 4. Third, this disproportionated, charge- and orbital-ordered ferromagnetic IF is half metallic (and thus not insulating).
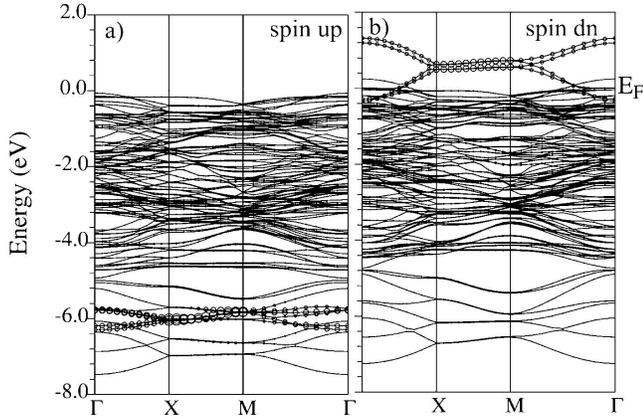
FIG. 4. Spin resolved LDA+U band structure of the oxygen states in the p-type LaAlO$_3$-SrTiO$_3$ interface with FM order of the oxygen holes. States localized near one of the magnetic oxygen ions in the AlO$_2$ layer of predominantly P_π hole character (see text) are emphasized with circles; these correspond to (a) lower (majority) and (b) upper (minority) Hubbard bands.

AFM ordering of hole spins. Now we consider the intuitively likely antiferromagnetic (AFM) ordering of the holes. We obtain the same charge- and square-symmetry broken solution as for FM order, except the near neighbor holes have their spins antialigned. Unlike the collective FM state, the AFM aligned hole, which is pictured in Fig. 5, is localized nearly completely on the central O$^*_{Al}$ ion, with a moment of $0.68\mu_B$. The higher degree of localization is reflected in the band structure plot in Fig. 6, and corresponds to the very flat unoccupied upper Hubbard P_π band that is almost entirely O$^*_{Al}$ p_y character. The separation between upper and lower Hubbard band, 7.5 eV, is slightly larger than in the FM ordered case.

Neglecting the very small splitting (~ 0.1 eV) of the upper Hubbard band due to interaction between the two IFs in the cell, which would vanish for more separated IFs, there is a gap of roughly 50 meV. The bandwidth is of the same order. From the tight-binding parameters of the FM upper Hubbard band, one would expect the nearest neighbor hopping to vanish (due to the U_p=7 eV splitting of states of the same spin for neighboring holes), but in addition the second neighbor hopping has dropped substantially ($t_2 \approx 6$ meV, versus 25 meV for the FM case). This change is another manifestation of the much stronger localization of the hole for AFM order. Thus for the AFM-ordered polaron lattice we obtain an insulating solution consistent with the small gap insulating behavior reported by Ohtomo and Hwang.[4] However, we point out that for the same U_p value the (unrelaxed) half-metallic ferromagnetic solution is by 0.15 eV more favorable than the insulating AFM. The more localized hole in the AFM case may provide a larger exchange energy gain, but the partial occupation of the dispersive minority upper Hubbard band may tip the balance for FM order. Relaxation of the positions of the neighboring ions may be larger for the more localized AFM ordered case, possibly resulting in energetic stabilization of the AFM insulating phase.

B. Charge compensation through oxygen vacancies

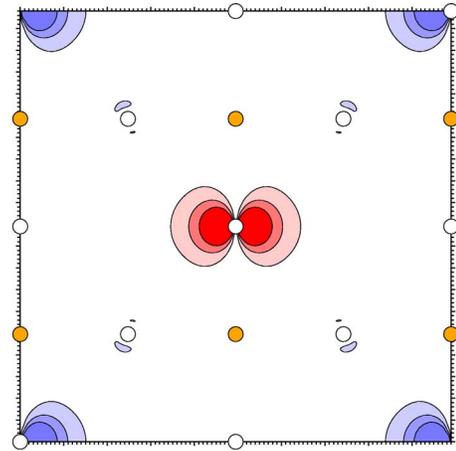In a recent publication Nakagawa, Hwang, and Muller[12] proposed that the p-type IF is compensated by oxygen de-

FIG. 5. (Color online) Charge density plot of the antiferromagnetically aligned p_y oxygen holes confined in the AlO$_2$ layer, illustrating the P_π hole state. The figure contains the simulated $p(2 \times 2)$ supercell, the positions of O and Al atoms are marked by white and orange (gray) circles, respectively. Holes in the majority (minority) spin channels localized at O$^*_{Al}$ at (0.0,0.0) and (0.5,0.5) are colored blue (gray) and red (dark gray), respectively.

fects. To investigate whether oxygen vacancies can render an explanation for the insulating behavior we have studied the two cases of a $p(2 \times 2)$ pattern of oxygen vacancies, either in the AlO$_2$ or in the SrO layer. Removing a neutral oxygen atom from an O^{2-} site leaves two electrons in the vicinity of the vacancy. If they stay localized in bulk, they form an optically active F center. At this interface vacancies should be energetically favored with respect to bulk vacancy formation because they can accommodate and compensate the holes that are intrinsic to this charge-imbalanced IF.

In both choices of vacancy site we find that the Fermi level lies in a narrow dip of the density of states (Figs. 7 and 9). There is no magnetism, and when the (small) interaction between the two interfaces in the cell is removed, both vacancy sites give an insulating result. Both positionings (SrO layer, or AlO$_2$ layer) of vacancies at the IF result in unoccupied states appearing within the bulk band gap. However, these states have differences in character for the two cases. For the vacancy in the AlO$_2$ layer the states immediately above E_F have density in the vacant site combined with $2p_\sigma$ character (with respect to the vacancy) of the oxygen ions neighboring the vacancy. The spatial distribution of the hole in the SrO layer and perpendicular to it is shown in Fig. 8. This type of state constitutes a charge-conjugate F center, into which electrons may be excited optically from the valence bands.

Although the vacancy in the SrO layer also compensates the holes with a generally similar charge-conjugate F center, the character of the F-center state on atoms neighboring the vacancy is quite different. The Ti ion neighboring the vacancy is missing its apex O ion, and this strongly rearranges the crystal field distribution of the 3d states. Ti d_{z^2} character lies lowest and is mixed into the F-center state, as pictured in Fig. 9. The entire set of 3d orbitals is lowered by ~ 2 eV relative to the further lying Ti, nearly filling the gap locally as can also be seen in Fig. 9(c).[27,28]
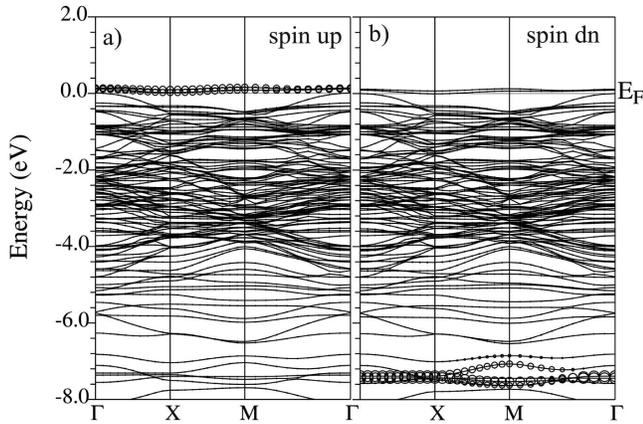
FIG. 6. Spin resolved band structure of the oxygen states in the p-type LaAlO$_3$-SrTiO$_3$ interface with AFM order of the oxygen holes. States localized near one of the magnetic oxygen ions in the AlO$_2$ layer of predominantly P_π hole character (see text) are emphasized with circles; these correspond to (a) upper (majority) and (b) lower (minority) Hubbard bands.

V. THE n-TYPE INTERFACE

Now we turn to the n-type IF which shows a qualitatively different mechanism of charge compensation of the extra half an electron per metal ion in the LaO-TiO$_2$ layer. Within GGA the electron goes into Ti $3d$-dominated conduction bands and the IF layer is a ferromagnetic metal with $M_{Ti}=0.19\mu_B$ distributed among the t_{2g} states. One clue to the response of this IF has been provided by Maurice and collaborators,[29] who have imaged an elongation of the unit cell at this IF. They interpret this distortion as an electronic response analogous to the Jahn-Teller effect leading to an asymmetric population of the Ti t_{2g} states. We return to this question below.

Since the LaO-TiO$_2$ unit forms the building block of the Mott-insulator LaTiO$_3$, we have applied LDA+U to this sys-
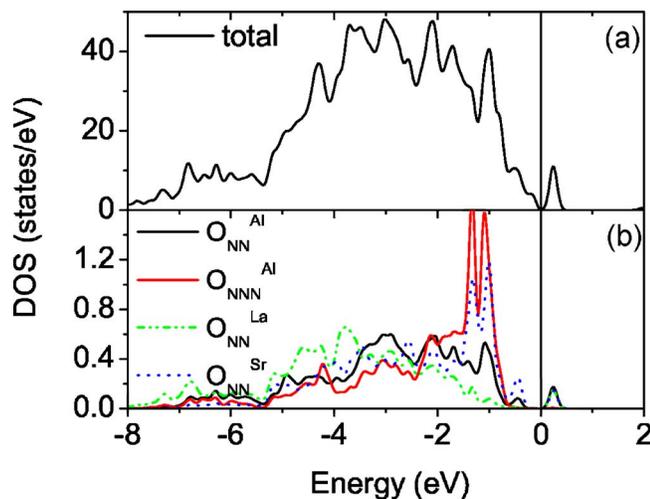

FIG. 7. (Color online) Density of states of the interface with an oxygen vacancy in the AlO$_2$ layer: (a) total; (b) projected DOS of the O $2p$ states of the oxygens surrounding the vacancy. Most of the density of the unoccupied gap state lies in the vacancy (see the text).
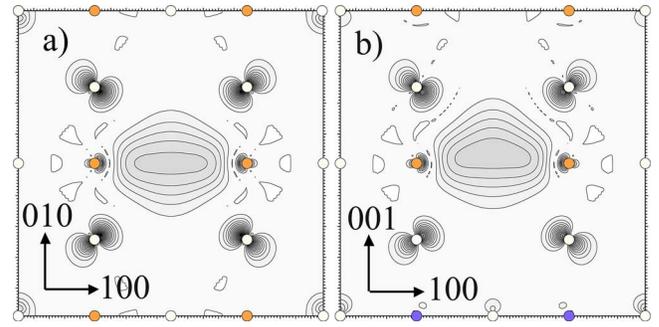

FIG. 8. (Color online) Charge density distribution of the unoccupied O $2p$ states around an oxygen vacancy in the AlO$_2$ layer. (a) and (b) show a cut through the xy and xz planes, respectively, with the vacancy positioned at (0.5, 0.5). The positions of O, Al, and Ti ions are marked by white, orange (gray), and blue (dark gray) circles, respectively.

tem, with $U_d=8$ eV on the Ti $3d$ states being the value that is needed to obtain an insulating AFM state for undistorted LaTiO$_3$. For a $c(2\times2)$ simulation cell, the ground state has an insulating band structure, with one narrow band split off below the other conduction bands (Fig. 10). The valence charge- (also spin-) density is that of disproportionated, checkerboard charge-ordered (Ti^{4+}+Ti^{3+}) localized in-plane d_{xy} electrons shown in Fig. 11. While bulk LaTiO$_3$ is an antiferromagnet of G-type with $M_{Ti}=0.73\mu_B$, at this n-type IF the Ti^{3+} spin-half moments couple ferromagnetically, with $M_{Ti^{3+}}=0.71\mu_B$ (Ti^{4+} have a very small moment of $0.05\mu_B$). Thus, while LaAlO$_3$ and SrTiO$_3$ are nonmagnetic materials, ferromagnetic order may be realized at the n-type IF due to charge imbalance.

The effect of this charge ordering on the Ti $3d$ states is substantial. In bulk, the (GGA) gap of SrTiO$_3$ is 3.2 eV. At this IF, the d_{xy} state is pulled into the gap, split off from d_{xz} and d_{yz} states by 4–5 eV. This would be an example of orbital order, except that the t_{2g}-degeneracy has already been broken by the asymmetry at the IF: four Sr^{2+} on one side, four La^{3+} ions on the other side of the Ti ion. This asymmetry, and the occupation of the d_{xy} orbital, result in a large splitting of the e_g pair. The unoccupied $3d$ states on the Ti^{3+} ion all lie 3 eV higher than on the Ti^{4+} ion.

Maurice et al.[29] reported an elongation of the unit cell on the LaTiO$_3$ side of the interface by 4.9%. In the present study we have not addressed atomic relaxations. Still, we find that the t_{2g} symmetry is already strongly lifted by asymmetric cations around the Ti ion. The occupation of the d_{xy} state alone separates it further from the $\{d_{xz}, d_{yz}\}$ pair, so the Jahn-Teller picture is not an appropriate one from which to approach this symmetry-breaking.

The insulating behavior obtained here seems at first glance to be at odds with the measured high conductivity.[4] With half the Ti sites empty, however, and fluctuation effects more pronounced in two dimension than in three, hopping to neighboring sites will be a frequent process even at relatively low temperature. In fact, this IF is a close realization of the quarter-filled two-dimensional Hubbard model, which is understood to be conducting at any nonzero temperature. The actual magnitude of the conductivity remains an open ques-
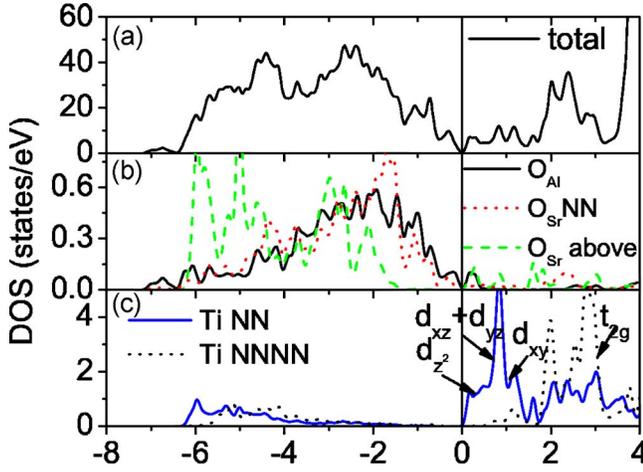
FIG. 9. (Color online) Density of states of the interface with an oxygen vacancy in the SrO layer: (a) total; (b) projected DOS of the O $2p$ states of the oxygen atoms surrounding the vacancy in the AlO$_2$ (black), SrO (red, short dashed), as well as in the next SrO layer on top of the vacancy (green, long dashed); (c) d states of the next (blue, solid) and third (black, dashed) Ti neighbor.

tion, but O vacancies are known to induce high mobility carriers, and superconductivity[30] in SrTiO$_3$. The charge disproportionation that we predict should be observable as a Curie-Weiss susceptibility of the accompanying spin, whether or not the FM order survives fluctuation effects to order at low temperature.

Lattice relaxations provide another possible explanation of the observed conductivity. At the interface between LaTiO$_3$ and SrTiO$_3$, which shows a similar mechanism of charge disproportionation to accommodate the excess electron, we have found that in the relaxed system the Fermi level shifts to lower energies and crosses the d_{xy} band at the Ti^{3+} sites leading to conducting (and half-metallic) behavior while still preserving the charge ordered arrangement.[31]

VI. SUMMARY

To provide a plausible picture of the observations of Ohtomo and Hwang[4] of SrTiO$_3$-LaAlO$_3$ IFs we have applied on-site repulsion U_p on O ions for the p-type IF, as well as the now accepted use of U_d for transitions metal ions for the n-type IF. For the more perplexing p-type IF, a value of $U_p = 7$ eV produces an intricate phase: disproportionation on the O sublattice (resulting in charge-polarons) of the AlO$_2$ layer, with the localized $S = \frac{1}{2}$ hole residing on an in-plane p_π-orbital, charge-ordered in a 2×2-fashion. Antiferromagnetic ordering of the spins finally produces an insulating phase. The strong localization of the O$_{Al}^*$ hole suggests this state may not require U_p as large as 7 eV for its stabilization. As an alternative possibility we have explored a charge compensation mechanism through O vacancies. Whether in the AlO$_2$ or the SrO layer, the hole resides in the vacant site F-center-like resulting in an insulating interface.

At the n-type IF the extra electron is localized but able to hop on the quarter-filled sublattice of Ti d_{xy} orbitals. Lattice relaxations are expected to lead to a half-metallic behavior
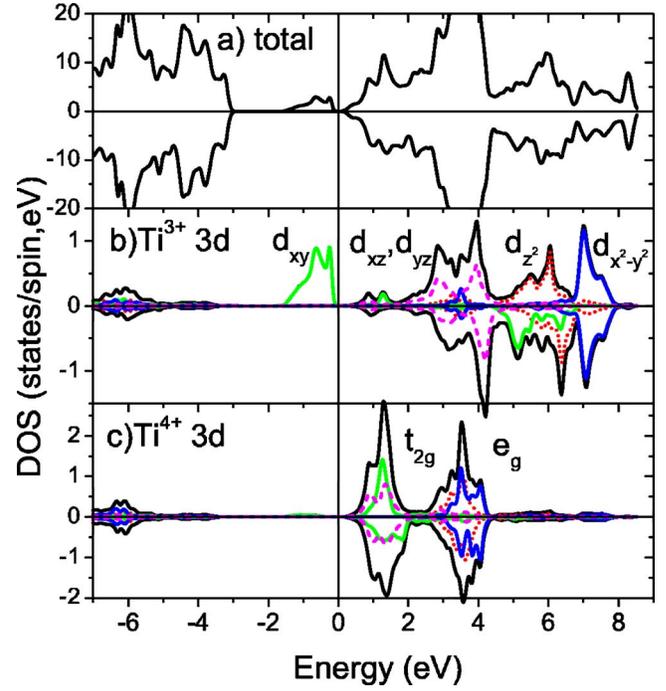

FIG. 10. (Color online) Density of states of the n-type interface: (a) total; (b) d states of magnetic Ti^{3+} showing the split-off majority d_{xy} band, with the corresponding minority states lying at +5 eV; the other $3d$ states are not strongly polarized; (c) the nonmagnetic Ti^{4+} ion, showing the conventional (although not perfect) $t_{2g} - e_g$ crystal field splitting. d_{xy} orbitals are marked by a green (light gray) line, d_{xz} and d_{yz} states by a magenta dashed line, states with d_{z^2} and $d_{x^2-y^2}$ character by a red dotted and blue (dark gray) solid lines, respectively.

and explain the measured conductivity. The ferromagnetically coupled layer realized at the interface of two nonmag-
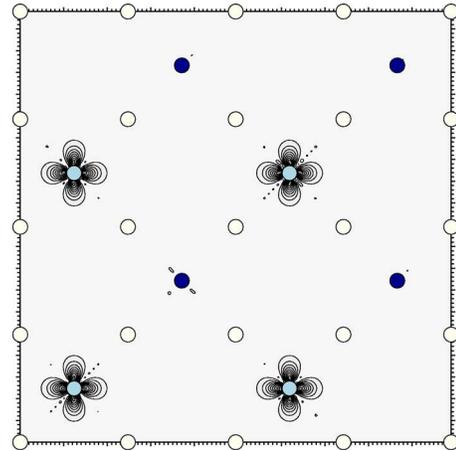

FIG. 11. (Color online) Charge density plot of the charge ordered state localized in the TiO$_2$ layer of the n-type interface. Ti^{3+} with an occupied d_{xy} orbital and Ti^{4+} marked by light and dark blue (gray) circles, respectively, are ordered in a (45°) checkerboard manner. Oxygens are marked by white circles. The plotted area corresponds to four $c(2 \times 2)$-simulation cells.

netic bulk materials opens up new possibilities, e.g., for spintronics applications and we hope that our result will motivate new experiments.

This investigation represents only a beginning of material-specific studies of abrupt oxide interfaces. Several limitations should be recognized. Our results, as with any mean-field band structure method, are for the ground state only, and temperature effects are not included. The LDA+U method in itself is not *ab initio*, since the value of U_p introduces some uncertainty, and the functional itself is simply a first step in taking account of correlation effects. Finally, treatment of correlations (especially at nonzero temperatures) will require dynamic effects such as are included in the dynamical mean field approach, and also intersite correlations describing ordering tendencies, which lie beyond even a dynamical mean field treatment.

The most intriguing aspect of our work is that we are raising the possibility that charge mismatch at the interface may drive strongly correlated electron behavior (charge disproportionation, local moments, and charge, spin, and orbital order) in O $2p$ bands when charge carriers are doped in (in this case, when holes are "grown into" the material). Probably the most robust aspect of our scenario is the local moment of the localized hole, which we expect to be insensitive to a small density of imperfections, for example. Magnetic measurements on these multilayer samples should provide the means to test our predictions, and thereby add to the understanding of these new nanoscale structures.

[1] J. N. Eckstein and I. Bozovic, MRS Bull. **19**, 44 (1994).

[2] A. Ohtomo, D. A. Muller, J. L. Grazul, and H. Y. Hwang, Nature (London) **419**, 378 (2002).

[3] H. Yamada, Y. Ogawa, Y. Ishii, H. Sato, M. Kawasaki, H. Akoh, and Y. Tokura, Science **305**, 646 (2004).

[4] A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).

[5] Y. Ijiri, J. Phys.: Condens. Matter **14**, R947 (2002).

[6] S. Okamoto and A. J. Millis, Phys. Rev. B **70**, 075101 (2004).

[7] E. Pavarini, S. Biermann, A. Poteryaev, A. I. Lichtenstein, A. Georges, and O. K. Andersen, Phys. Rev. Lett. **92**, 176403 (2004).

[8] G. A. Baraff, J. A. Appelbaum, and D. R. Hamann, Phys. Rev. Lett. **38**, 237 (1977).

[9] S. Gallego, J. I. Beltran, J. Cerda, and M. C. Munoz, cond-mat/0509578 (unpublished).

[10] I. S. Elfimov, S. Yunoki, and G. A. Sawatzky, Phys. Rev. Lett. **89**, 216403 (2002).

[11] X. Wan, M. Kohno, and X. Hu, Phys. Rev. Lett. **95**, 146602 (2005).

[12] N. Nakagawa, H. Y. Hwang, and D. A. Muller, Nat. Mater. **5**, 204 (2006); cond-mat/0510491 (unpublished).

[13] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Univ. Wien, Austria, 2001. ISBN 3-9501031-1-2.

[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).

[16] Because only about 65%–70% of the density of an occupied O $2p$ orbital lies within the atomic sphere ($n_{2p}^{up/dn}=0.7$), and it is only this density that the U correction is applied to, to achieve an effective $U_{\text{eff}}=U\ n_{2p}^{up/dn}=7$ we have used $U=10$ eV as input to WIEN2k.

[17] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[18] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).

[19] M. S. Hybertsen, N. E. Christensen, and M. Schlüter, Phys. Rev. B **39**, 9028 (1989).

[20] I. A. Nekrasov, M. A. Korotin, and V. I. Anisimov, cond-mat/0009107 (unpublished).

[21] S. Ray, P. Mahadevan, A. Kumar, D. D. Sarma, R. Cimino, M. Pedio, L. Ferrari, A. Pesci, Phys. Rev. B **67**, 085109 (2003).

[22] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. **40**, 964 (1978).

[23] L. F. Feiner, J. H. Jefferson, and R. Raimondi, Phys. Rev. B **53**, 8751 (1996).

[24] V. I. Belinicher and A. L. Chernyshev, Phys. Rev. B **49**, 9746 (1994).

[25] A. J. W. Reitsma, L. F. Feiner, and A. M. Oleś, cond-mat/0507169 (unpublished).

[26] L. D. Landau, Phys. Z. Sowjetunion **3**, 644 (1933).

[27] K. Shibuya, T. Ohnishi, M. Kawasaki, H. Koinuma, and M. Lippmaa, Jpn. J. Appl. Phys., Part 2 **43**, L1178 (2004).

[28] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, Phys. Rev. B **38**, 11322 (1988).

[29] J.-L. Maurice, C. Carretero, M.-J. Casanove, K. Bouzehouane, S. Guyard, E. Larquet, and J.-P. Contour, cond-mat/0511123 (unpublished).

[30] J. F. Schooley, W. R. Hosler, and M. L. Cohen, Phys. Rev. Lett. **12**, 474 (1964).

[31] R. Pentcheva and W. E. Pickett (unpublished).