Correlation-Driven Charge Order at a Mott Insulator - Band Insulator Digital Interface

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To study digital Mott insulator LaTiO\textsubscript{3} and band insulator SrTiO\textsubscript{3} interfaces, we apply correlated band theory (LDA+U) to (n,m) multilayers, 1 \leq n, m \leq 9. If the on-site repulsion on Ti is large enough to model the magnetic insulating behavior of cubic bulk LaTiO\textsubscript{3}, the charge imbalance at the interface is found in all cases to be accommodated by disproportionation (Ti\textsuperscript{4+} + Ti\textsuperscript{3+}), charge ordering, and Ti\textsuperscript{3+} \textit{d}_{xy}\textit{-orbital ordering, with antiferromagnetic exchange coupling between the spins in the interface layer. Lattice relaxation affects the conduction behavior by shifting (slightly but importantly) the lower Hubbard band, but the disproportionation and orbital ordering are robust against relaxation.

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Atomically abrupt (“digital”) interfaces (IFs) between oxides with strongly differing electronic properties (superconducting-ferromagnetic; ferroelectric-ferromagnetic) have attracted interest\textsuperscript{1, 2} due to the new behavior that may arise, and for likely device applications. Hwang and collaborators\textsuperscript{3-5} have reported coherent superlattices containing a controllable number of Mott insulator [LaTiO\textsubscript{3} (LTO)] and band insulator [SrTiO\textsubscript{3} (STO)] layers using pulsed laser deposition, with analysis suggesting atomically sharp interfaces comparable to those produced by molecular beam epitaxy\textsuperscript{6}. The most provocative result was that the IFs of these insulators showed metallic conductivity and high mobility. Electron energy loss spectra (EELS) for Ti suggested a superposition of Ti\textsuperscript{3+} and Ti\textsuperscript{4+} ions in the interface region. Incorporating doping with magnetic ions, these same materials are being explored for spin-dependent transport applications\textsuperscript{7, 8, 9}. Effects of structural imperfections are being studied\textsuperscript{3, 7, 8, 9}, but the ideal IFs need to be understood first.

Single- and three-band Hubbard models with screened intersite Coulomb interaction have been applied to this IF. Both the Hartree-Fock approximation or dynamical mean field with a semiclassical treatment of correlation\textsuperscript{10} result in a ferromagnetic (FM) metallic IF over a substantial parameter range. \textit{Ab initio} studies reported so far have focused on charge profiles\textsuperscript{11, 12} while neglecting correlation effects beyond the local density approximation (LDA) that we address below. Very recent \textit{ab initio} calculations of the effects of lattice relaxation\textsuperscript{12, 13} at the IF have provided additional input into the Hubbard-modeling of these IFs, allowing the investigation of the interplay of correlation effects and relaxation in these models.

The material-specific insight into correlated behavior that can be obtained from first-principles-based approaches is still lacking. In LTO/STO superlattices, the transition metal ions on the perovskite B-sublattice are identical (Ti) and only the charge-controlling A-sublattice cations (Sr, La) change across the interface\textsuperscript{14} (cf. Fig. 1). This leaves at each IF a TiO\textsubscript{2} layer whose local environment is midway between that in LTO and STO. In this paper we study mechanisms of charge compensation at the LTO/STO-IF based on density-functional theory calculations\textsuperscript{15, 16, 17} within the general-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Segment of the (1,1) LaTiO\textsubscript{3}-SrTiO\textsubscript{3} multilayer, illustrating the cubic perovskite structure (unlabeled white spheres denote oxygen). An LaO layer lies in the center, bordered by two TiO\textsubscript{2} layers, with a SrO layer at top and bottom. The lateral size of this figure corresponds to the \textit{p}(2 \times 2) cell discussed in the text.}
\end{figure}

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ized gradient approximation (GGA) [15] employing the all electron FP-LAPW-method within the WIEN2k-implementation [16] including a Hubbard-type on-site Coulomb repulsion (LDA+U) [17]. We focus on (1) the local charge imbalance at the IF and its dependence on neighboring layers, (2) the breaking of three-fold degeneracy of the Ti $t_{2g}$ orbitals which will be at most singly occupied, (3) magnetic ordering and its effect on gap formation, and (4) how rapidly the insulators heal (both in charge and in magnetic order) to their bulk condition away from the IF.

To explore the formation of possible charge disproportionated, magnetically ordered, and orbitally selective phases at the IF and to probe the relaxation length towards bulk behavior we have investigated a variety of $(n,m)$ heterostructures with $n$ LTO and $m$ STO layers $(1 \leq n,m \leq 9)$, and lateral cells of $c(2 \times 2)$ or $p(2 \times 2)$ [14]. The $\hat{z}$ direction is taken perpendicular to the IF. Lattice parameters of the systems have been set to the experimental lattice constant of STO, 3.92 Å, therefore modeling coherent IFs on an STO substrate. Bulk STO is a semiconductor with a GGA-band gap [15] of 2.0 eV (experimental value 3.2 eV), separating filled O 2$p$ bands from empty Ti 3$d$ bands.

Currently LTO ($a=3.97$ Å) and other 3$d^1$ perovskites are intensively studied because their structure is crucial in determining their electronic and magnetic behavior [15]. Bulk LTO is an AFM insulator of G-type (rocksalt spin arrangement) with a gadolinium orthoferrite (20 atom) structure; however, lattice imaging indicates that only a few layers of LTO assume the cubic structure that we use in our superlattices. Using the LDA+U method, an AFM insulator is obtained for $U \geq 6$ eV, with a magnetic moment $M_{Ti} \approx 0.75 \mu_B$ due to occupation of one of the $t_{2g}$ orbitals (orbital ordering arising from spontaneous symmetry breaking). FM alignment of spins is 50 meV/Ti less favorable. We discuss first the (1,1) multilayer (1LTO/1STO) layer pictured in Fig. 4 and then consider systems with thicker LTO and/or STO slabs to analyze the relaxation towards bulk behavior.

The (1,1) superlattice is modeled in a transverse $c(2 \times 2)$ cell (not considered in earlier work [13]) with two inequivalent Ti ions, which allows disproportionation within a single Ti layer and is consistent with the AFM G-type order in bulk LTO. The on-site repulsion strength $U$ on Ti was varied from 0 to 8 eV to assess both weak and strong interaction limits. The Ti moment versus $U$ and the evolution of the density of states as a function of $U$ are shown in Fig. 2a) and b), respectively. Within GGA ($U = 0$) nonmagnetic metallic character is obtained, consistent with earlier reports. [11, 12] For $U \leq 5$ eV the system is a ferromagnetic metal with equivalent Ti ions, i.e., it is qualitatively like earlier results on multiband Hubbard models. [11] At $U \approx 5.5$ eV disproportionation occurs on the Ti ions, apparently weakly first-order as has been found to occur in the Na$_2$CoO$_2$ system [15]. Around $U \approx 6$ eV there is a half metallic ferromagnet region, but beyond $U \approx 6.5$ eV a gap opens separating the lower Hubbard band and resulting in a correlated insulator phase. In the following we model the Mott insulating gap (0.5 eV) with $U=8$ eV.

The arrangement of disproportionated ions, which is charge-ordered (CO) rocksalt, retains inversion symmetry and, more importantly, the more highly charged $d^0$ ions avoid being nearest neighbors. The spatial distribution of the occupied $d$-orbitals in the IF TiO$_2$ layer displayed in Fig. 4 reveals that besides the CO for $U > 7$ eV this state is orbitally ordered (OO) with a filled $d_{xy}$ orbital at the Ti$^{3+}$ sites, the non-degenerate member of the cubic $t_{2g}$ triplet after the intrinsic symmetry-lowering effect of the IF. The Fermi level lies in a small Mott gap separating the occupied narrow $d_{xy}$ band (‘lower Hubbard band’) from the rest of the unoccupied $d$-orbitals. For ferromagnetic alignment of the spins ($M_{Ti^{3+}} = 0.72 \mu_B$) the gap ensures an integer moment ($2.0 \mu_B$).

The system at this level of treatment is a realization of a quarter-filled extended Hubbard model
p(2×2)-cell to allow antiferromagnetic alignment of the 
Ti$^{3+}$ spins. We obtain the same CO/OO state with 
the Ti ions in (n,m) superlattices. Due to the c(2×2)-
lateral unit cell there are two inequivalent Ti-ions in each 
layer. (n,m) denotes a multilayer containing n LTO and 
m STO layers. The IF moments are nearly bulk-like 
and become so at the layer next to the IF layer. (1,5)$^*$ 
denotes a configuration where the interlayer distances 
were relaxed according to Ref.[13].

| System $(n,m)$ | LTO | IF-2 | IF-1 | IF | IF+1 | IF+2 |
|---------------|-----|------|------|---|------|------|
| (1,1)         | -   | -    | -    | 0.72/0.05 | - | -   |
| (1,5)         | -   | -    | -    | 0.71/0.05 | 0.0/0.0 | 0.0/0.0 |
| (1,5)$^*$     | -   | -    | -    | 0.50/0.08 | 0.0/0.0 | 0.01/0.01 |
| (5,1)         | 0.73/-0.73 | -0.73/0.73 | 0.70/0.05 | - | -   |
| (5,5)         | 0.73/-0.73 | -0.73/0.73 | 0.70/0.06 | 0.0/0.0 | 0.0/0.0 |

The (n,m) superlattice. To examine charge- and 
spin-order relaxation towards bulk behavior, and ob-
serve charge accommodation at more isolated IFs, 
we have studied several thicker slabs containing 
(n,m) layers of LTO and STO, respectively, with 
1 ≤ n, m ≤ 9. Following the experiment of Ohtomo 
et al.[3] we present results specifically for the (1,5) 
and (5,1) as well as the (5,5) superlattices, all of 
which we find to be disproportionated, CO and OO, 
and insulating in the strong interaction regime. As 
is clear both from the layer-resolved magnetic 
moments presented in Table I and the layer resolved 
projected DOS for the (1,5) superlattice in Fig. 4a), 
the IF TiO$_2$ layer, and only this layer, is CO/OO 
with Ti$^{3+}$ and Ti$^{4+}$ distributed in a checkerboard 
manner. At every second Ti-site the $t_{2g}$ states 
split according to the IF-imposed symmetry low-
ering, and the $d_{xy}$ orbital becomes occupied. The 
t$_{2g}$ states on the Ti$^{4+}$ ions remain essentially de-
gerate, and there is only a tiny induced moment $M_{Ti^{3+}} = 0.06\mu_B$. Ti ions in neighboring or deeper 
layers in the STO part of the slab have the con-
figuration 3d$^0$ and are nonmagnetic, while those on 
the LTO side of the slab have the configuration 3d$^1$
and are AFM G-type ordered. Thus the charge 
mismatch is localized at the interface layer, with

FIG. 4: Layer-resolved density of states of a) struct-
urally ideal and b) relaxed (1,5) multilayer. The two 
topmost panels show Ti$^{3+}$ and Ti$^{4+}$ at the IF, 
the succeeding panels show the behavior of the Ti-ion in deeper 
layers of the STO part of the slab. While for the ideal 
geometry rapid relaxation of the electronic structure to 
bulk form versus distance from the interface (IF) takes 
place, in the relaxed structure the electronic relaxations 
involve deeper lying layers.
bulk LTO and STO character quickly re-emerging on neighboring layers. Consequently, these results indicate a relaxation length much less that the 1-2 nm value estimated from the EELS data. The same CO/OO results have been obtained on a variety of \((n, m)\) LTO-STO superlattices; these repeatedly emerging insulating ordered IF phases are very robust.

However, the systems discussed so far are structurally perfect with ideal positions of the atoms in the perovskite lattice. In the following we discuss the influence of lattice relaxations on the electronic properties of the system. Recently, two DFT studies using GGA [12] and the LDA+U approach [13] investigated structural relaxations in LaTiO\(_3\)/SrTiO\(_3\) superlattices, finding that Ti-ions at the IF are displaced by 0.15 Å with respect to the oxygen ions leading to a longer Ti-Ti distance through the LaO layer than through the SrO-layer. This “ferroelectric”-like distortion decays quickly in deeper lying layers. Using the relaxations reported in Ref. [13], we repeated the calculations for the (1,5)-heterostructure. The resulting layer-resolved projected DOS at the Ti-ions is displayed in Fig. 4b). The most prominent feature is that for the relaxed structure the \(d_{xy}\)-band (the lower Hubbard band) has been shifted up by 0.4 eV, leaving it incompletely (\(\sim 70\%\)) occupied. The charge is distributed in the minority spin channel at the Ti\(^{3+}\)-sites (hybridization with O2p bands) reducing the magnetic moment from 0.71\(\mu_B\) in the ideal structure to 0.50\(\mu_B\). Additionally there is a small contribution to conductivity of Ti\(^{4+}\) in deeper lying layers in the SrTiO\(_3\)-host whose \(d\)-bands now slightly overlap the Fermi level. Hence it is the lattice relaxations that result in a metallic heterostructure and a longer healing length towards bulk behavior, in agreement with the experimental observations [3, 4] in spite of a majority of the charge being tied up at the IF. Still, the CO/OO arrangement remains; it is robust with respect to relaxation and tetragonal distortion.

Now we summarize. While the behavior of the many superlattices that we have studied produce robust results for the IFs which is easily understood, they have a charge- and orbital-ordered character that was unanticipated from the original reports on these heterostructures. If the interaction strength \(U\) within the Ti 3\(d\) states is large enough to reproduce the AFM insulating state in cubic LTO, then it is more advantageous for the local charge imbalance to be accommodated within the IF layer itself, which can be accomplished by disproportionation, followed by charge order with Ti\(^{3+}\) and Ti\(^{4+}\) distributed in a checkerboard manner. The interface layer is orbitally-ordered, with an occupied \(d_{xy}\)-orbital; this symmetry breaking is due to the intrinsic IF symmetry and is unaffected by atomic relaxation. Indeed both disproportionation and orbital ordering are insensitive to relaxation. For the ideal structure, the CO/OO state is a very narrow gap insulator. In agreement with previous studies, [12, 13] coupling to the lattice is however found to be important in some respects. Most notably, atomic relaxation at the IF shifts the Ti\(^{3+}\) lower Hubbard band upward just enough to lead to conducting behavior, which also implies a longer healing length towards bulk behavior, consistent with the experimental indications.

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