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

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To study digital Mott insulator $LaTiO_3$ and band insulator $SrTiO_3$ 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 Mott insulating behavior of cubic bulk $LaTiO_3$, the charge imbalance at the interface is found in all cases to be accommodated by disproportionation (Ti^{4+} + Ti^{3+}), charge ordering, and Ti^{3+} d_{xy}-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[1, 2] due to the new behavior that may arise, and for likely device applications. Hwang and collaborators [3, 4] have reported coherent superlattices containing a controllable number of Mott insulator [$LaTiO_3$ (LTO)] and band insulator [$SrTiO_3$ (STO)] layers using pulsed laser deposition, with analysis suggesting atomically sharp interfaces comparable to those produced by molecular beam epitaxy [1]. 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^{3+} and Ti^{4+} ions in the interface region. Incorporating doping with magnetic ions, these same materials are being explored for spin-dependent transport applications [5]. Effects of structural imperfections are being studied [6–9], 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 [10] result in a ferromagnetic (FM) metallic IF over a substantial parameter range. *Ab initio* studies reported so far have focused on charge profiles or lattice relaxations [11, 12] while neglecting correlation effects beyond the local density approximation (LDA) that we address below. Very recent LDA+U calculations focussed on the effect of lattice relaxations providing additional input into the Hubbard-modeling [13] of this system.

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 (*cf.* Fig. 1). This leaves at each IF a TiO_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 [within the generalized gradient approximation (GGA) [14]] employing the all electron FP-LAPW-method within the

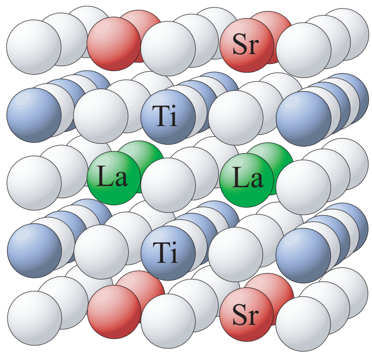

FIG. 1: Segment of the (1,1) $LaTiO_3$-$SrTiO_3$ multilayer, illustrating the cubic perovskite structure (unlabeled white spheres denote oxygen). An LaO layer lies in the center, bordered by two TiO_2 layers, with a SrO layer at top and bottom. The lateral size of this figure corresponds to the $p(2 \times 2)$ cell discussed in the text.

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WIEN2k-implementation [15] including a Hubbard-type on-site Coulomb repulsion (LDA+U) [16]. 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 ($1 \leq n, m \leq 9$). We have considered additional degrees of freedom that have not been addressed in a theoretical investigation so far by using lateral cells of $c(2\times2)$ or $p(2\times2)$ [17]. 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 [14] of 2.0 eV (experimental value 3.2 eV), separating filled O $2p$ bands from empty Ti $3d$ bands.

Currently LTO (a=3.97 Å) and other $3d^1$ perovskites are intensively studied because their structure is crucial in determining their electronic and magnetic behavior [18]. 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. 1, 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 $c(2\times2)$ 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. [10] 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_xCoO_2 system [19]. 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. 3 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

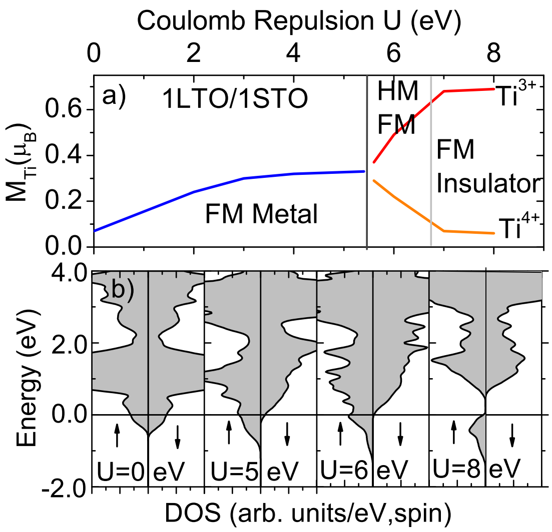

FIG. 2: a) Phase diagram of the Ti moments for the (1,1) superlattice in a transverse $c(2 \times 2)$ cell, versus the on-site Coulomb repulsion strength U on the Ti $3d$ orbitals. b) Density of states (spin direction indicated by arrows) of the (1,1) superlattice for different U values. Disproportionation occurs in a weak first-order manner around $U \approx$5.5 eV. HM FM indicates a region of half metallic ferromagnetism before the Mott gap appears around $U \approx 6.5$ eV.

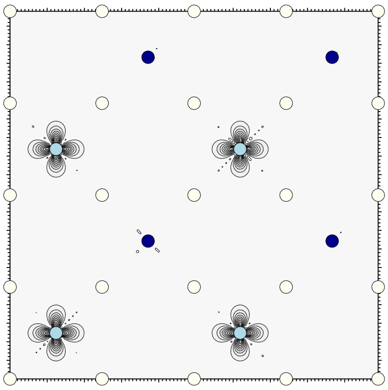

FIG. 3: 45° checkerboard charge density distribution of the occupied $3d$ states in the charge-ordered TiO_2 layer in the FM (1,1) multilayer. Orbital-ordering due to d_{xy} orbital occupation is apparent. The positions of O-, Ti^{3+} and Ti^{4+}-ions are marked by white, dark blue (black) and light blue (grey) circles, respectively.

(EHM) system. The Hubbard model itself is metallic at quarter-filling; when intersite repulsion is included [20, 21] it becomes CO and insulating. The intersite repulsion is included correctly in first principles methods and that combined with the on-site repulsion (U) gives charge ordering.

The calculation was extended to a larger $p(2\times2)$-cell to allow antiferromagnetic alignment of the Ti^{3+} spins. We obtain the same CO/OO state with an occupied d_{xy}-orbital on every second IF Ti ion, giving a checkerboard ordering of Ti^{3+} and Ti^{4+}, regardless of whether the spins are aligned or antialigned. AFM coupling is preferred by 80 meV per $p(2\times2)$-cell for the (1,1) superlattice (a spin-spin exchange coupling of $|J|$=10 meV). For heterostructures containing a thicker LTO slab, however, AFM coupled spins on the 50% diluted p(2×2) mesh in the IF layer will not match the AFM G-type order on the LTO side of the slab, where spins in the IF-1 layer couple antiparallel with a c(2×2)-periodicity. Due to this frustration, AFM alignment within the IF layer may become less favorable.

The (n,m) superlattice. To examine charge- and spin-order relaxation towards bulk behavior, and observe charge accommodation at more isolated IFs, we have studied several thicker slabs containing (n,m) layers of LTO and STO, respectively, with $1 \le n,m \le 9$. 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),

TABLE I: Layer resolved magnetic moments (in μ_B) of the Ti ions in (n,m) superlattices. Due to the $c(2\times2)$-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	LTO		IF	STO	
(n,m)	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 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 lowering, and the d_{xy} orbital becomes occupied. The t_{2g} states on the Ti^{4+} ions remain essentially degenerate, and there is only a tiny induced moment $M_{Ti^{4+}} = 0.06\mu_B$. Ti ions in neighboring or deeper layers in the STO part of the slab have the configuration $3d^0$ 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

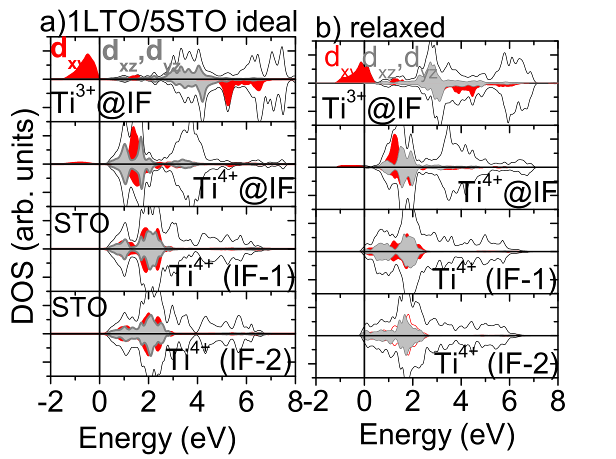

FIG. 4: Layer-resolved density of states of a a) structurally ideal and b) relaxed (1,5) multilayer. The two topmost panels show Ti^{3+} and Ti^{4+} at the IF, the succeeding panels show the behavior of the Ti-ion in deeper layers of the STO part of the slab. While for the ideal geometry rapid relaxation 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 [3].

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 0.15Å 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. If the interaction strength U within the Ti 3d states is large enough to reproduce the AFM insulating state in cubic LTO, charge mismatch at $LaTiO_3/SrTiO_3$-superlattices is found to be compensated within the IF layer itself by disproportionation, followed by charge order with Ti^{3+} and Ti^{4+} distributed in a checkerboard manner. Already the symmetry breaking at the interface (and not lattice relaxations) invokes orbital-order in the IF layer, with an occupied d_{xy}-orbital at the Ti^{3+}-sites. This charge and orbital order emerging robustly in all systems studied is easily understood but unanticipated from the original reports on these heterostructures and could only be obtained by an explicit and self-consistent treatment of electronic correlation and additional degrees of freedom (larger lateral periodicity) not considered so far. 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. The magnetic state at these IFs is also unexpected - while bulk $SrTiO_3$ is nonmagnetic and $LaTiO_3$ is an antiferromagnet, at these IFs we find a diluted layer of Ti^{3+}-ions spins (due to lack of spin on the Ti^{4+} sites) whose exchange coupling is AFM in sign.

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range as the Ti 3d states. Although both orbitals are quite localized and there is no hybridization between them, we have used $U_{\mathrm{La}} = 7.5$ eV to shift the empty f-states to higher energies.
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