Electron correlation and magnetism at the LaAlO$_\text{3}$/SrTiO$_\text{3}$ interface: An DFT+DMFT investigation

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We study the metallic character and the magnetic order observed in heterostructures based on the bulk band insulators LaAlO$_{3}$ and SrTiO$_{3}$. The realistic interface electronic structure is computed by using the (spin-polarized) charge self-consistent combination of density functional theory (DFT) with dynamical mean-field theory (DMFT) beyond the realm of static correlation effects. While many-body behavior appears also in the defect-free case, a ferromagnetic instability occurs only with oxygen vacancies at the interface. There a minimal Ti two-orbital $e_{g}$-$t_{2g}$ description for the correlated subspace is derived. Ferromagnetism affected by quantum fluctuations builds up from effective double exchange between tailored nearly-localized $e_{g}$ and quasi-itinerant $xy$ electrons.

The interface physics that emerges from alloying the bulk band insulators LaAlO$_{3}$ (LAO) and SrTiO$_{3}$ (STO) is a key highlight in the prominent research on oxide heterostructures (see e.g. $^1$,$^2$ for a review). Crystal growth along [001] results in a metallic two-dimensional electron system (2DES) for an AlO$_{2}$-LaO-TiO$_{2}$ (n-type) boundary region $^{3,4}$. Since that stacking direction formally leads to a diverging electrostatic potential with increasing thickness, electronic reconstruction to avoid the polar catastrophe $^{5}$ is one possible explanation for the 2DES. Intrinsic doping via oxygen vacancies $^{6,7}$ may also play a role, their relevance for itineracy at a vacuum-cleaved STO surface has been demonstrated $^{8}$. Surprisingly, ferromagnetic (FM) and superconducting order $^{9,12}$ may be stabilized in LAO/STO heterostructures. The ferromagnetism is either specific to the stoichiometric interface $^{13}$ or is associated with the occurrence of defects $^{14}$. In any case, electron correlations are assumed to be important for the fascinating phenomenology. Coexistence of itinerant and localized electrons is suggested from scanning-tunneling spectroscopy $^{15,16}$, anisotropic magnetoresistance and anomalous Hall effect measurements $^{17}$, resonant soft-x-ray scattering $^{18}$ as well as photoemission $^{19}$.

Numerous theoretical works address metallicity and magnetism of the LAO/STO interface 2DES, ranging from model-Hamiltonian studies $^{20,25}$ to density functional theory (DFT) (+Hubbard U) investigations $^{2,26}$, $^{24}$. Though agreement exists about focusing the Ti(3$d$) shell, differences concerning crucial sub-shell states and the relevance of crystal defects persist. Because of low Ti filling at stoichiometry, there sole local Coulomb correlations are not expected sufficient for phenomenology-relevant many-body physics $^{20,22}$. Inspired by DFT+U calculations with interface oxygen vacancies $^{26}$, Pavlenko et al. used a basic $e_{g}$-$t_{2g}$ Hubbard model $^{24}$ to consider the itinerant/localized signature in Hartree-Fock. Ruhman et al. rely on a defect-induced $t_{2g}$-only description within a Kondo-model scope $^{27}$. From the existing works however a realistic many-body revelation of the actual itinerant low-energy orbital-spin state in conjunction with the question about the necessary degree of stoichiometry remains open.

In this study the interplay of structure and electron correlation in supporting metallicity and ferromagnetism at realistic LAO/STO interfaces is assessed by means of the charge self-consistent DFT + dynamical mean-field theory (DMFT) approach. We show that the defect-free case exhibits correlation signatures, but can be ruled out for promoting FM order based on local self-energies. The key correlated subspace of the oxygen-vacancy-hosting interface problem is directly cast into a minimal Ti two-orbital description near quarter filling. Effective double exchange between an almost-localized tailored $e_{g}$ state and a coexisting quasi-itinerant $t_{2g}(xy)$ level then drives an intricate FM phase subject to quantum fluctuations.

A superlattice including four layers of LAO(STO), each with two in-plane unit cells, models the n-type interface (see Fig. 1a). This setup is just above the minimal LAO thickness-limit for the onset of ferromagnetism $^{28}$. To study the impact of defects on the LAO/STO physics, two extreme interface cases are constructed. A defect-free (DF) one and an oxygen-vacancy-hosting (HV) one with high defect concentration. One O vacancy per interface is placed in the boundary TiO$_{2}$ layer. Asymmetric vacancy positions are chosen to reduce defect coherency. With 25% vacancies per interface TiO$_{2}$ usual experimental magnitudes are exceeded, but the modelling is geared to grasp the key doping effect. Three inequivalent TiO$_{2}$ layers, each with two Ti ions, are identified. One may inplane symmetrize each Ti pair, but Ti$^{(1)}$, Ti$^{(2)}$ as well as Ti$^{(3)}$, Ti$^{(4)}$ are treated inequivalent to account for possible strong intra-laver ordering tendencies.

A metallic state is revealed for both structure types from DFT in the local density approximation (LDA) (see Fig. 1b). At stoichiometry, two electrons occupy the dominant Ti(3$d$) low-energy manifold, matching the number for polar-catastrophe avoidance, which predicts Ti$^{3.5+}$O$_{2}^{2-}$ at the interface $^{3}$. Six electrons settle in the Ti(3$d$)-like manifold with vacancies. There the occu-
Correlated orbitals are absent in the far-from-interface Ti ions (see Fig. 1b). Small weight without fluctuation to free states may be neglected. It follows (e_g, t_2g) for Ti^{12}\) and t_2g for Ti^{34}, Ti^{5} (=Ti^{345}). Abandoning five-orbital schemes, a three-orbital construct seems proximate, since only xz is t_2g-sizeable on Ti^{12}. But a three-orbital z^{2}, x^{2}−y^{2}, x\_xy projection of the low-energy LDA bands yields strong hybridization between the two e_g orbitals. This was already suggested from the directed \(\rho_0(e_g)\) weight in Fig. 2b. Diagonalizing the local-projected \(z^{2}−x^{2}−y^{2}\) Hamilton matrix reduces the e_g problem to a single relevant e_g orbital on each Ti^{12} ion (see Fig. 2c). We retrieve a two-orbital (e_g, x\_xy) correlated subspace in the interface TiO\_2 layer, similar to what was used in 24. A respective two-orbital subspace is also sufficient on the remaining Ti ions due to the alike behavior of xz and yz. Thus a symmetrized xz/yz orbital projection together with xz\_xy is constructed for Ti^{345}. To incorporate the tailored correlated subspace in a true many-body framework, charge self-consistent DFT+DMFT 35 37 is build up on the orbital projection from 30 Kohn-Sham bands following the Ti(3d)-like manifold’s lower band edge 33. At each Ti site a rotational-invariant multi-orbital Hubbard Hamiltonian based on Slater-Kanamori parameterization, i.e. Hubbard U and Hund’s exchange \(J_H\), is applied (see su-

![FIG. 1. (color online) (a) Ideal 4\_2 LAO/STO structure: La (large orange/lightgrey), Sr (large blue/grey), Al (small green/grey), O (small red/dark) ions and symmetry-equivalent Ti ions. Small dark circles mark O vacancies. (b,c) LDA data after structural relaxation: (b) band structure and (c) orbital-resolved DOS of projected Ti(3d) orbitals. Data for Ti^{2}(Ti^{4}) is identical to Ti^{1}(Ti^{3}) (see text).](image)

![FIG. 2. (color online) (a,b) LDA bonding charge density \(\rho_{b}^{(LDA)}=\rho_{tot}^{(LDA)}−\rho_{atomic}^{(LDA)}\) for VH \(4\_2\) LAO/STO. (a) Ti^{5}O_2 layer and (b) interface Ti^{12}O_2. (c) Ti two-orbital basis with average levels from projected onsite Kohn-Sham Hamiltonian. The e_g orbital reads \(|\psi_{e_g}| \sim 0.55|x|^2 ± 0.84|y^2+y|^2\).](image)
Computing $U$, $J_H$ from first principles is tough for the complicated crystal structures. Therefore we pick the values suitably to provide access to the key LAO/STO correlation physics. Though $3d$ orbitals on inequivalent sites occur, for simplicity site-independent Coulomb interactions are chosen. For a three-orbital modelling of bulk titanates $U \sim 5$ eV, $J_H \sim 0.7$ eV is a proper choice \[38\]. Since here weakly correlated LaAlO$_3$ participates and orbital-reduced schemes are applied, we lower the values to moderate $U=3.5(2.5)$ eV and $J_H=0.5$ eV for the three(two)-orbital case \[13, 24\]. For the whole supercell, five inequivalent impurity problems are solved at each step of full DFT+DMFT \[37\], utilizing the hybridization-expansion version of continuous-time quantum Monte Carlo \[39–42\]. Computations are performed at temperature $T=145.1$K ($\beta=1/T=80$eV$^{-1}$), if not otherwise stated. A double-counting correction of the fully-localized form \[43\] is applied.

Though weakly filled (see Tab. I), the stoichiometric DF interface is susceptible to local Coulomb correlations. Figures 3a,b show a sharp quasiparticle (QP) peak and small-scale spectral-weight transfer dominantly for $xy$ which is singled out by orbital polarization. By comparison, the VH paramagnetic (PM) energy spectrum displays still richer correlation signatures. Apart from substantial low-energy renormalization Fig. 3c reveals a shallow lower Hubbard band.

This incoherent excitation stems dominantly from the two $e_g$-like bands, as verified by the $T_i^{(1)}$ impurity spectral function (cf. Fig. 3a). The peak position at $\sim -1.2$ eV is in excellent agreement with photoemission data \[19\]. A QP peak in favor of $xy$ but additional $e_g$ weight completes the itinerancy/localization dichotomy mainly originating within the $T_i^{(12)}$ layer. Orbital-based differences in the interface effective-mass are noted by $1/Z_{xy}=m^*(xy)/m_{LDA}(xy) \sim 1.3$, in good accordance with Shubnikov-de Hass measurements \[44\], and $1/Z_{\epsilon_g}=m^*(\epsilon_g)/m_{LDA}(\epsilon_g) \sim 2.1$. Mass renormalization for $T_i^{(345)}$ $t_{2g}$-like states is rather weak. From Tab. I a single electron is associated with each $T_i^{(12)}$ ion in the VH case. Roughly 3/4 therefrom are of stronger-localized $\epsilon_g$ and 1/4 of stronger-itinerant $xy$ character. Significiant charge disproportionation between $T_i^{(1)}$ and $T_i^{(2)}$ is not observed. The spectral function $A(k, \omega)$ in Fig. 4a reveals DMFT self-energy-induced shifts of spectral weight (see supplementary) compared to the LDA bands (Fig. 1b). A flattened $xy$-like QP band starts right below the Fermi level at $\Gamma$. That shifted low-filled $xy$-like QP band carries also $T_i^{(5)}$ weight, i.e. away from the direct interface region. Therefore lowest-energy QP bands around $\Gamma$ are not only associated with interface-nearest ($T_i^{(12)}$) electrons. The hybridized $\epsilon_g/xy$ band close to $M$ rests at $\epsilon_F$, about forming a hole pocket. Originally weakly dispersing bands along $\Gamma$–$X$ have shorter lifetime and the $\epsilon_g$- and $xz/yz$-like bands appear now partly merged.

Albeit numerically demanding, no conclusive net FM magnetic moment can be deduced for the DF structure within DFT+DMFT. However allowing for FM spin polarization in the VH case leads to magnetic order, nearly

![FIG. 3.](image)

![FIG. 4.](image)

**TABLE I.** Local $T_i^{(3d)}$ fillings in DF and VH structure from DFT+DMFT. DF: averaged $xz, yz$ and $xy$ values. VH: ($\epsilon_g, xy$) on $T_i^{(12)}$ and ($xz/yz, xy$) on $T_i^{(345)}$.**

|        | $T_i^{(1)}$ | $T_i^{(2)}$ | $T_i^{(3)}$ | $T_i^{(4)}$ | $T_i^{(5)}$ |
|--------|-------------|-------------|-------------|-------------|-------------|
| DF PM  | 0.02 0.16   | 0.02 0.16   | 0.07 0.05   | 0.07 0.05   | 0.08 0.04   |
| PM PM  | 0.76 0.24   | 0.79 0.24   | 0.15 0.06   | 0.17 0.06   | 0.24 0.04   |
| VH FM  | 0.41 0.19   | 0.43 0.19   | 0.07 0.03   | 0.08 0.03   | 0.12 0.02   |
| PM FM  | 0.36 0.06   | 0.36 0.07   | 0.07 0.02   | 0.08 0.02   | 0.12 0.02   |
FIG. 5. (color online) Im $\Sigma(i\omega_n)$ of Ti$^{(1)}$ impurity self-energy in VH case. Lines are from 5th-order polynomial interpolation in a larger frequency range. (a) PM data at various $T$ (insets: blow up close to $\omega=0^+$). (b) Data at $T=145.1K$.

exclusively located in the Ti$^{(12)}$O$_2$ layer (cf. Tab. I). The FM phase is indeed lower in energy, but the difference to the PM phase is small, i.e. $\sim$10 meV/Ti$^{(12)}$. A small local Ti$^{(12)}$ moment of $\sim$0.09$\mu_B$ is detected, in excellent agreement with experiment $^{12}$. Notably this moment builds up from polarizing both local orbitals, yet surpris-ingly $\epsilon_g$, though lower filled, has a larger share. The real-space spin contrast shown in Fig. 4a underlines that finding. At $\varepsilon_F$, electrons are either of $\epsilon_g$ spin-down or close-to spin-average $t_{2g}$ (only Ti$^{(12)}$ $xy$ contribution shown) flavor (see Fig. 3b). Thus the FM state in LAO/STO has a truly intriguing itinerant signature, emerging from many-body scattering between QPs and nearly-localized electrons. The spectral spin contrast in Fig. 5 renders the fact obvious that major spin polarization is tied to low-energy. The correlation-induced exchange splitting leads to a modified fermiology, especially close to the M point, where a spin-down QP band with substantial $\epsilon_g$ weight finally forms a hole pocket. The interplay of the computed renormalized spin-up and -down bands at low-energy will be relevant for the observed low-$T$ coexistence of ferromagnetism and superconductivity $^{11}$.

Since the PM spectral intensity at $\varepsilon_F$ is enhanced with correlations, the Stoner criterion rewritten for the Hubbard model as $UA(\varepsilon_F)>1$ is fulfilled. Furthermore it is known that the Hund’s exchange $J_H$ triggers itinerant ferromagnetism in the orbital-degenerate two-band Hubbard model close to quarter filling $^{45, 46}$. Especially here due to the vacancy-induced localization/itinerancy dichotomy $J_H$-driven double-exchange (DE) processes should account for the main part of the underlying mechanism. However a distinct orbital-character separation into localized spin and itinerant electrons as in the standard DE model Hamiltonian is not fully ade-quate. Figure 5 displays the temperature dependence of the PM Ti$^{(1)}$ self-energy part Im $\Sigma(i\omega_n)$ for Matsubara frequencies $\omega_n=(2n+1)\pi T$. Besides showing the noted orbital differentiation in the QP renormaliza-
tion $Z=(1 - \partial I m \Sigma(\omega)/\partial \omega |_{\omega \rightarrow 0^+})^{-1}$ it reveals insight in the electron-electron scattering ($\sim$ Im $\Sigma(0^+)$) for $\epsilon_g$, $xy$. The more localized $\epsilon_g$ electrons are less coherent at higher $T$. Consistent with a DE-like mechanism the coherency in the FM phase at low temperature is higher than in the PM phase (see Fig. 4a). Magnetic scattering is reduced in the spin-polarized medium due to the satisfaction of the Hund’s term. From charge self-consistent DFT+DMFT in the FM phase now using the spin-averaged charge density in the DFT part we encounter significantly reduced Ti$^{(12)}$ moments around $T=290K$. In line with experimental findings $^{12}$, the Curie temperature of ferromagnetic LAO/STO may thus roughly estimated to lie somewhat above room temperature.

In summary, by applying realistic many-body theory to a defect-free and a vacancy-hosting supercell structure, we reveal various ingredients and characteristics of metallicity and ferromagnetism at the LAO/STO interface. Local Coulomb interactions create correlations in the DF interface electronic structure. However within DFT+DMFT those are not strong enough to cause an FM state or straightforward charge-ordering instabilities. Note that static correlation effects based on DFT+U also yield FM moments in the VH case $^{21}$, but with too large magnitude compared to experiment. Realistic quantum fluctuations are efficient in reducing the Ti interface moment down to the experimental value of $\sim$0.1$\mu_B$ $^{13}$. Furthermore they account for strongly renormalized $T$-dependent QPs as well as incoherent spectral weight. The basics of the many-body behavior may be under-stood within a minimal two-orbital $\epsilon_g$-$xy$ picture. It orig-i-nates in the nearest-interface TiO$_2$ layer and is here de-vised from the full supercell electronic structure. Double-exchange processes between more localized $\epsilon_g$ and more itinerant $xy$ lead to ferromagnetism. The intricate fermi-ology of especially the FM state involves at least two ($\epsilon_g$, $xy$) carrier types. Details on charge transfers, or-bital contributions, etc. still ask for an inclusion of Ti states from more distant TiO$_2$ layers. Note finally that here two extreme structural cases, i.e. stoichiometric and with high vacancy concentration, are studied. In reality a more sophisticated intermediate situation is likely, but the qualitative aspects due to vacancies elucidated in this work are believed to remain vital.

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Supplemental Information

DETAILS ON CRYSTAL STRUCTURE AND CALCULATIONAL PROCEDURE

The supercell used in the present work for both structures is based on 80 atomic sites. We utilize the SrTiO$_3$ (STO) lattice constant $a=3.905\AA$ in the planes perpendicular to the $c$ axis, while the $c/a$ ratio is optimized to $c/a=0.986$ for the whole cell from total-energy minimization. In general the local $c/a$ is somewhat larger unity in the STO part, whereas its below unity in the LaAlO$_3$ (LAO) part. Local structural relaxation allowed for the defect-free (DF) and the vacancy-hosting (VH) structure is performed by minimizing the atomic forces within the local density approximation (LDA). A mixed-basis pseudopotential scheme is utilized for the LDA calculations. Using localized functions for Ti($3d$) and O($2s2p$) in the Kohn-Sham basis renders it possible to reduce the plane-wave cutoff energy to moderate $13$ Ryd for the large cell. Up to an $9\times 9\times 3$ tailoring is used for the $k$-point mesh in reciprocal space.

The local interacting problem on each individual Ti site is described by the many-body Hamiltonian

$$
\mathcal{H} = U \sum_m n_{m\uparrow}n_{m\downarrow} + \frac{1}{2} \sum_{m\neq m',\sigma} \left\{ U' n_{m\sigma}n_{m'\bar{\sigma}} + U'' n_{m\bar{\sigma}}n_{m'\sigma} + J_H \left( c_{m\sigma}^{\dagger}c_{m'\bar{\sigma}}c_{m'\sigma}c_{m\bar{\sigma}} + c_{m\sigma}^{\dagger}c_{m'\bar{\sigma}}c_{m'\bar{\sigma}}c_{m\sigma} \right) \right\},
$$

with orbital index $m$, spin projection $\sigma=\uparrow, \downarrow$ and $n=c^{\dagger}c$. It is parametrized by the Coulomb integral $U$ and the Hund’s exchange $J_H$ with $U'=U-2J_H$ and $U''=U-3J_H$. The charge self-consistent DFT+DMFT framework is used for solving the realistic interacting problem. Note that in principle a combined two-orbital Ti$^{(12)}$ and three-orbital Ti$^{(345)}$ (with then site-dependent Hubbard $U$) treatment for the VH case would also be possible within our DFT+DMFT coding. However since we do not expect significant $xz$ or $yz$ polarization we choose the symmetrized $xz/yz$ description on Ti$^{(345)}$.

In the spin-polarized ferromagnetic case, the Kohn-Sham part is handeled within the local spin density approximation (LSDA) and the complete spin-resolved charge density is converged. Only for a rough estimation of the Curie temperature $T_c$ for the VH structural case the spin-averaged charge self-consistency DFT+DMFT cycle with however of course spin-resolved DMFT self-energies is utilized.

KOHN-SHAM HAMILTONIAN AND DFT+DMFT LEVEL SHIFTING

There are 10 Ti ions in the supercell. With our choices concerning the respective correlated subspace, the complete projected Kohn-Sham Hamiltonian has thus the dimension $30\times 30$ for the DF calculation and $20\times 20$ for the VH one. For instance, the inplane nearest-neighbor $(NN)$ Ti$^{(12)}$ Hamiltonian block in the latter case reads

$$
H_{c_{xy}}^{(KS,12,NN)} = \begin{pmatrix}
T_i^{(1)} & T_i^{(1)} & T_i^{(2)} & T_i^{(2)} \\
416 & 0 & -204 & 0 & -2 & 0 \\
0 & 729 & 0 & 0 & 180 & 0 \\
-1 & 0 & 416 & 0 & -2 & 161 & 0 \\
0 & 0 & 0 & 729 & 0 & 0 & -247 \\
-204 & 0 & 2 & 397 & 0 & -1 & 0 \\
0 & 180 & 0 & 0 & 728 & 1 & 0 \\
-2 & 0 & 161 & 0 & -1 & 397 & 0 \\
0 & 0 & 0 & -247 & 0 & 0 & 728
\end{pmatrix}
$$

whereby each onsite Ti subblock consists of a $2\times 2$ matrix for $c_{xy}$ and $c_{yz}$ and the values are given in meV.

Besides band renormalization and spectral-weight transfer with correlations, the real part $\text{Re}\Sigma(i0^+)$ of the local self-energy introduces a level shifting. The additional crystal-field splitting $\Delta_c$ due to many-body effects is computed as $\Delta_c=\varepsilon_{\text{CSC}}+\text{Re}\Sigma(i0^+)-\Delta_{\text{DC}}-\varepsilon_{\text{KS}}$ for each involved local electronic state individually. Here $\varepsilon_{\text{CSC}}$ is the converged local level energy from the KS-like part within DFT+DMFT, $\Delta_{\text{DC}}$ is the orbital-independent but site-dependent shift from the fully-localized double counting and $\varepsilon_{\text{KS}}$ the original Kohn-Sham level energy within LDA. Table II shows the resulting correlation-induced level shifting for the projected orbitals in the VH structural case. Note that the coherent part of all shifts is of course absorbed in the chemical potential determined at each DFT+DMFT step.

| $\varepsilon_{\text{KS}}$ | $\Delta_c$ |
|-----------------|--------|
| 416 729         | 244 160 |
| 397 728         | 249 146 |
| 865 1016        | 191 240 |
| 903 1016        | 200 250 |
| 870 1086        | 279 372 |

TABLE II. Kohn-Sham levels and correlation-induced shifting $\Delta_c$ (in meV) for (left) $c_{xy}$ and (right) $c_{yz}$, respectively, in the VH structure within DFT+DMFT at $T_c=145.1K$. 

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**Note:** The table and text contain mathematical expressions and matrices that are not fully rendered in the text format. The full context and equations are best read in their native format (LaTeX, etc.).