

Electron correlation and magnetism at the LaAlO₃/SrTiO₃ interface: A DFT+DMFT investigationFrank Lechermann,¹ Lewin Boehnke,¹ Daniel Grieger,² and Christoph Piefke¹¹*Institut für Theoretische Physik, Universität Hamburg, D-20355 Hamburg, Germany*²*International School for Advanced Studies (SISSA), Via Bonomea 265, I-34136 Trieste, Italy*

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We shed light on the interplay between structure and many-body effects relevant for itinerant ferromagnetism in LaAlO₃/SrTiO₃ heterostructures. The realistic correlated electronic structure is studied by means of the (spin-polarized) charge self-consistent combination of density-functional theory with dynamical mean-field theory beyond the realm of static correlation effects. Though many-body behavior is also active in the defect-free interface, a ferromagnetic instability occurs only with oxygen vacancies. A minimal Ti two-orbital e_g - t_{2g} description for the correlated subspace is derived. Magnetic order affected by quantum fluctuations builds up from effective double exchange between modified nearly localized e_g and mobile xy electrons.

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I. INTRODUCTION

The interface physics emerging from the combination of LaAlO₃ (LAO) and SrTiO₃ (STO) bulk band insulators highlights the prominent research on oxide heterostructures (see, e.g., Refs. [1,2] for a review). Crystal growth along (001) results in a metallic two-dimensional electron system (2DES) for an AlO₂-LaO-TiO₂ (n-type) boundary region [3,4]. Since that stacking formally leads to a diverging electrostatic potential with increasing thickness, electronic reconstruction to avoid the polar catastrophe [5] is a possible explanation for the 2DES. Intrinsic doping via oxygen vacancies [6,7] may also play a role, as demonstrated in view of itinerancy at vacuum-cleaved STO surfaces [8]. Surprisingly, ferromagnetic (FM) and superconducting order [9–12] may be stabilized in LAO/STO interfaces. Ferromagnetism is either bound to stoichiometry [13] or associated with defects [14], but in any case, electron correlations are assumed to be important. Coexistence of itinerant and localized electrons is suggested from scanning-tunneling spectroscopy [15,16], anisotropic magnetoresistance, anomalous Hall effect measurements [17], resonant soft x-ray scattering [18], and photoemission [8,19,20].

Numerous theoretical works address the LAO/STO interface 2DES, ranging from model-Hamiltonian studies [21–27] to density-functional theory (DFT) (+Hubbard U) investigations [9,22,24,28,29]. Though agreement exists about focusing on the Ti(3d) shell, differences concerning crucial subshell 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 [21,23]. Inspired by DFT+ U calculations with interface oxygen vacancies [29], Pavlenko *et al.* used a basic e_g - t_{2g} Hubbard model [25] to consider the itinerant/localized signature in Hartree-Fock approximation. Other many-body modelings focus on defect-driven electronic states within an impurity/Kondo scope [26,27]. Yet a first-principles many-body revelation connecting (defect) structure, itinerant orbital-spin state, and ferromagnetism is still lacking.

We here remove this deficiency and reveal the subtle interplay between defect occurrence and many-body effects in supporting metallic ferromagnetism at realistic LAO/STO interfaces, based on a charge self-consistent DFT + dynamical

mean-field theory (DMFT) study. While local self-energies do not promote FM order in the defect-free case, with oxygen vacancies effective double exchange governed by the Hund exchange J_H near quarter filling drives an intricate FM phase subject to quantum fluctuations. The connected key correlated subspace is readily derived as being composed of vacancy-induced almost-localized tailored e_g and quasi-itinerant $t_{2g}(xy)$ states.

II. CRYSTAL STRUCTURE AND THEORETICAL FRAMEWORK

A superlattice with four LaO(SrO) layers, each having a $\sqrt{2} \times \sqrt{2}$ in-plane unit cell, models the n-type interface [see Fig. 1(a)]. This is just above the minimal LAO thickness limit for the onset of FM order [30]. The supercell is based on 80 atomic sites. We utilize the STO lattice constant $a = 3.905$ Å 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 it is below unity in the LAO part.

The impact of defects is examined from two interface limits: a defect-free (DF) case and an oxygen-vacancy-hosting (VH) one with high defect concentration. One O vacancy per interface is placed in the boundary TiO₂ layer [7,31,32]. Asymmetric vacancy positions are chosen to reduce defect coherency. The 25% vacancies per interface TiO₂ exceed usual experimental magnitudes, but the modeling is geared to grasp the key doping effect. Three inequivalent TiO₂ layers are identified. One may in-plane-symmetrize each in-plane Ti pair, but Ti⁽¹⁾, Ti⁽²⁾ as well as Ti⁽³⁾, Ti⁽⁴⁾ are treated inequivalent to allow for intralayer ordering tendencies.

The local structural relaxation allowed for the defect-free and the vacancy-hosting 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 a $9 \times 9 \times 3$ tailoring is used for the k -point mesh in reciprocal space. The two-dimensional Brillouin zone (BZ)

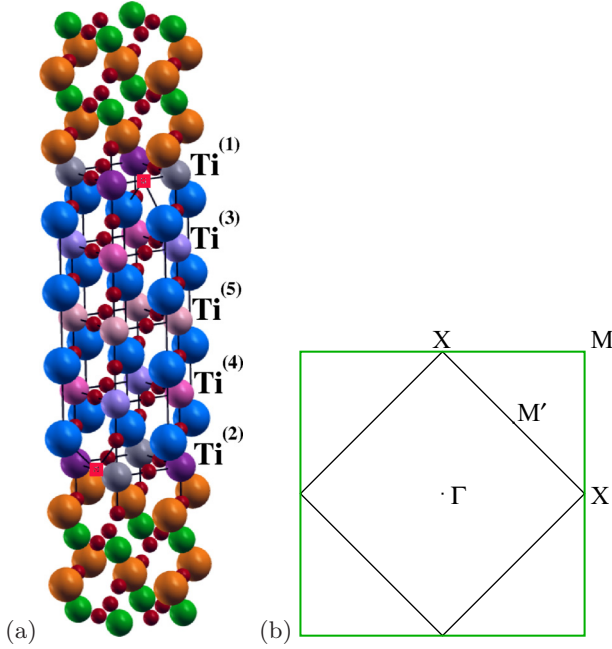


FIG. 1. (Color online) (a) Ideal LAO/STO structure: La [large orange (light gray)], Sr [large blue (gray)], Al [small green (gray)], O [small red (dark)] ions and symmetry-inequivalent Ti ions. Small squares mark O vacancies. (b) (k_x, k_y) Brillouin zone for the here used $\sqrt{2} \times \sqrt{2}$ structuring with two in-plane Ti atoms (black). The basic 1×1 BZ is given in green (gray). The high-symmetry points read $\Gamma = (0, 0, 0)$, $M' = (\frac{\pi}{4a}, \frac{\pi}{4a}, 0)$, $M = (\frac{\pi}{2a}, \frac{\pi}{2a}, 0)$, $X = (0, \frac{\pi}{2a}, 0)$.

of our enlarged in-plane unit cell is shown in Fig. 1(b). Note that the M' point discussed here is located half the distance to Γ compared to the original M of the basic square BZ for the single-atom square/cubic structure.

Charge self-consistent DFT+DMFT [33–35] is build on the derived orbital projection from 30 Kohn-Sham bands following the Ti(3d)-like manifold's lower band edge [36]. At each Ti site a rotational-invariant Slater-Kanamori parametrization of the multiorbital Hubbard Hamiltonian, i.e., Hubbard U and Hund's exchange J_H , is applied. The local interacting problem on each individual Ti site is described by the many-body Hamiltonian

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

with orbitals $m, m' = 1, 2, (3)$, spin projection $\sigma = \uparrow, \downarrow$, and $n = c^\dagger c$. Interorbital density-density terms scale with $U' = U - 2J_H$ and $U'' = U - 3J_H$. Computing U , J_H from first principles is tough for the complicated crystal structures. Therefore we choose suitable values to access key LAO/STO correlation physics, whereby the Coulomb interactions are approximated site independent. The values $U \sim 5$ eV, $J_H \sim 0.7$ eV are a proper choice [37] for three-orbital models of bulk titanates. Because of the weakly correlated LaAlO_3 part and the use of orbital-reduced schemes, we lower to moderate $U = 3.5$ (2.5) eV and $J_H = 0.5$ eV for the three-(two)-orbital case [15,25] (see Sec. IV). Five inequivalent

impurity problems are solved at each step of full DFT+DMFT [35] in the supercell, utilizing the hybridization-expansion version of continuous-time quantum Monte Carlo [38–41]. Computations are performed at temperature $T = 145.1$ K ($\beta \equiv 1/T = 80$ eV $^{-1}$), if not otherwise stated. A double-counting correction of the fully localized form [42] is applied. The maximum-entropy method is used for the analytical continuation from Matsubara space to obtain the spectral data.

In the spin-polarized ferromagnetic case, the Kohn-Sham part is handled 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 cycle with however of course *spin-resolved* DMFT self-energies is utilized.

III. LDA BAND STRUCTURE AND DENSITY OF STATES

Metallicity is obtained for both structure types from DFT in LDA (see Fig. 2). At stoichiometry, two electrons occupy the dominant Ti(3d) low-energy manifold, matching the number for polar-catastrophe avoidance, which predicts $\text{Ti}^{3.5+}\text{O}_2^{4-}$ at the interface [5]. Figure 2(a) shows that the two electrons which form the 2DES are confined to the STO part, with dominant localization near $\text{Ti}^{(2)}$, i.e., directly at the boundary towards the LAO part.

Six electrons settle in the Ti(3d)-like manifold with vacancies. There the occupied bandwidth amounts to ~ 0.5 eV, with two additionally filled bands along Γ - M' in the Brillouin zone. An orbital-character analysis renders these

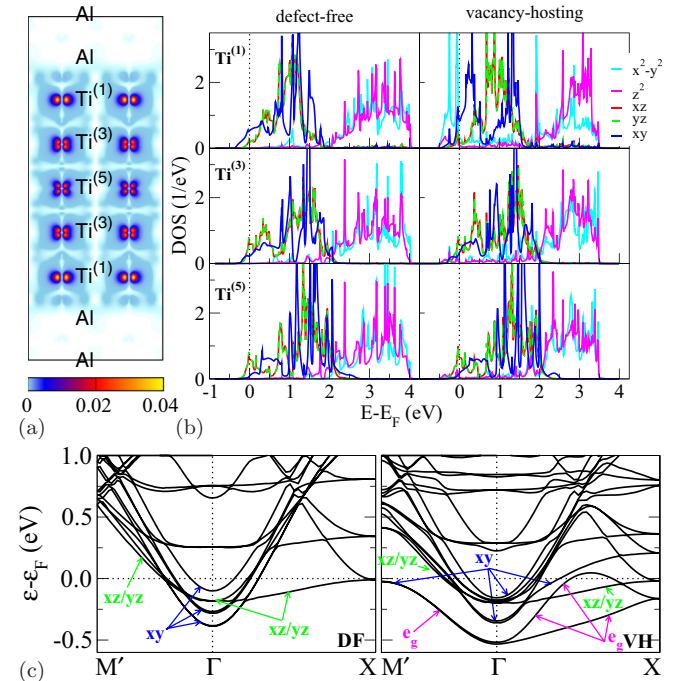


FIG. 2. (Color online) LDA data for LAO/STO. (a) Valence charge density of the occupied low-energy manifold in the DF structure. (b) Orbital-resolved DOS of projected Ti(3d). $\text{Ti}^{(2)}$ ($\text{Ti}^{(4)}$) data are identical to $\text{Ti}^{(1)}$ ($\text{Ti}^{(3)}$) data (see text). (c) Band structures along high-symmetry lines.

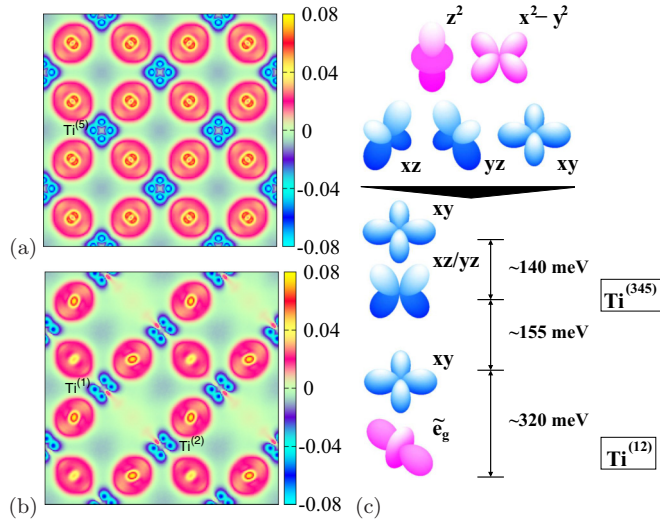


FIG. 3. (Color online) (a), (b) LDA bonding charge density $\rho_b^{(LDA)} = \rho_{\text{tot}}^{(LDA)} - \rho_{\text{atomic}}^{(LDA)}$ for VH 4×2 LAO/STO. (a) $\text{Ti}^{(5)}\text{O}_2$ layer and (b) interface $\text{Ti}^{(12)}\text{O}_2$. (c) Tailored Ti orbital basis derived from original $3d$ states along with average LDA level splittings. The \tilde{e}_g orbital reads $|\tilde{e}_g\rangle \sim 0.55|z^2\rangle \pm 0.84|x^2 - y^2\rangle$.

two bands e_g -like, yet with sizable xy weight close to M' . For the t_{2g} part the xz/yz -like bands have in general larger LDA effective mass than xy -like. The new bands are indeed associated with $\text{Ti}(e_g)$ states liberated from $\text{O}(2p)$, as also evident from the local $\text{Ti}(3d)$ -resolved density of states (DOS) [cf. Fig. 2(b)]. In real space, the LDA layer bonding charge density [Figs. 3(a), 3(b)] exhibits directly e_g -like filling of $\text{Ti}^{(1)}$, $\text{Ti}^{(2)}$ ($=\text{Ti}^{(12)}$) in addition to xy . The former share is absent in the far-from-interface $\text{Ti}^{(5)}\text{O}_2$ layer.

Spin-polarized LDA does not support ferromagnetism with a sizable supercell net moment ($m_{\text{tot}} \leq 0.01\mu_B$) for either structure type. That is corroborated by the failing Stoner criterion $IN(\epsilon_F) > 1$ in the DFT context [43] which should signal an itinerant FM state for Stoner parameter I and DOS $N(\epsilon_F)$ per Ti spin at the Fermi level. The value of I for elemental Ti is about 0.6 eV [44] and a computation directly for LAO/STO by Janicka *et al.* yields 0.725 eV [45]. Our obtained $N(\epsilon_F) = 0.63$ (0.77) eV^{-1} per spin for the DF (VH) interface are thus not sufficient to allow for conventional band magnetism.

IV. CORRELATED SUBSPACE

Correlations are important and we here treat those beyond existing static DFT+ U studies [28,29]. First we elaborate on the minimal correlated subspace [36,46,47] for the LAO/STO 2DES. An e_g - t_{2g} modeling is advocated from the LDA findings. However a complete correlated $3d$ -shell five-orbital description of $\text{Ti}^{(1-5)}$ is very challenging. Instead we devise a simpler approach guided by low-energy states.

For the DF interface a t_{2g} -based three-orbital correlated subspace for all Ti ions is adequate [see Fig. 2(b)]. The VH structure with its sharing e_g - t_{2g} spectral structure close to ϵ_F asks for more. Yet we only treat e_g character directly at the interface, i.e., only for $\text{Ti}^{(12)}$. Albeit there is some e_g leaking into the $\text{Ti}^{(34)}\text{O}_2$ layer, an *unoccupied* low-energy e_g part is

TABLE I. Local $\text{Ti}(3d)$ fillings in DF and VH structure from DFT+DMFT. DF: Averaged xz, yz , and xy values. VH: (\tilde{e}_g, xy) on $\text{Ti}^{(12)}$ and $(xz/yz, xy)$ on $\text{Ti}^{(345)}$.

| | | $\text{Ti}^{(1)}$ | | $\text{Ti}^{(2)}$ | | $\text{Ti}^{(3)}$ | | $\text{Ti}^{(4)}$ | | $\text{Ti}^{(5)}$ | |
|----|--------------|-------------------|------|-------------------|------|-------------------|------|-------------------|------|-------------------|------|
| DF | PM | 0.02 | 0.16 | 0.02 | 0.16 | 0.07 | 0.05 | 0.07 | 0.05 | 0.08 | 0.04 |
| | PM | 0.76 | 0.24 | 0.79 | 0.24 | 0.15 | 0.06 | 0.17 | 0.06 | 0.24 | 0.04 |
| VH | \uparrow | 0.41 | 0.19 | 0.43 | 0.19 | 0.07 | 0.03 | 0.08 | 0.03 | 0.12 | 0.02 |
| | \downarrow | 0.36 | 0.06 | 0.36 | 0.07 | 0.07 | 0.02 | 0.08 | 0.02 | 0.12 | 0.02 |

missing. Small weight without fluctuations to free states may be neglected. It follows (e_g, t_{2g}) for $\text{Ti}^{(12)}$ and t_{2g} for $\text{Ti}^{(34)}$, $\text{Ti}^{(5)}$ ($=\text{Ti}^{(345)}$). Abandoning five-orbital schemes, a three-orbital construct seems proximate, since only xy is t_{2g} -sizeable on $\text{Ti}^{(12)}$. But a three-orbital $z^2, x^2 - y^2, xy$ projection of the low-energy LDA bands yields strong hybridization between the two e_g orbitals. This was already suggested from the directed $\rho_b(e_g)$ weight in Fig. 3(b). Diagonalizing the local-projected $(z^2, x^2 - y^2)$ Hamiltonian matrix reduces the e_g problem to a single relevant \tilde{e}_g orbital on each $\text{Ti}^{(12)}$ ion [see Fig. 3(c)]. We retrieve a two-orbital (\tilde{e}_g, xy) correlated subspace in the interface TiO_2 layer, similar to what was heuristically used in Ref. [25]. 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 xy is constructed for $\text{Ti}^{(345)}$. Note that in principle a combined two-orbital $\text{Ti}^{(12)}$ and three-orbital $\text{Ti}^{(345)}$ treatment (with then site-dependent Hubbard U) for the VH case would also be possible within our DFT+DMFT coding. However since we do not expect significant xz vs yz polarization we choose the symmetrized xz/yz description on $\text{Ti}^{(345)}$.

V. MANY-BODY EFFECTS

Though weakly filled (see Table I), the stoichiometric DF interface is susceptible to Coulomb correlations within DFT+DMFT. Figures 4(a) and 4(b) show a sharp quasiparticle

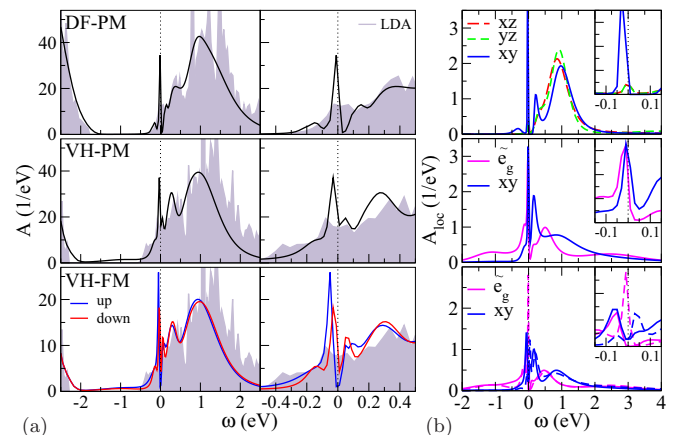


FIG. 4. (Color online) k -integrated DFT+DMFT spectral data. (a) Total spectrum including 30 states above $\text{O}(2p)$ - $\text{Ti}(3d)$ gap (right part: blow-up around ϵ_F). (b) $\text{Ti}^{(1)}$ impurity defect free (top) and vacancy-hosting PM (middle), FM (bottom, spin-down: dashed lines) data.

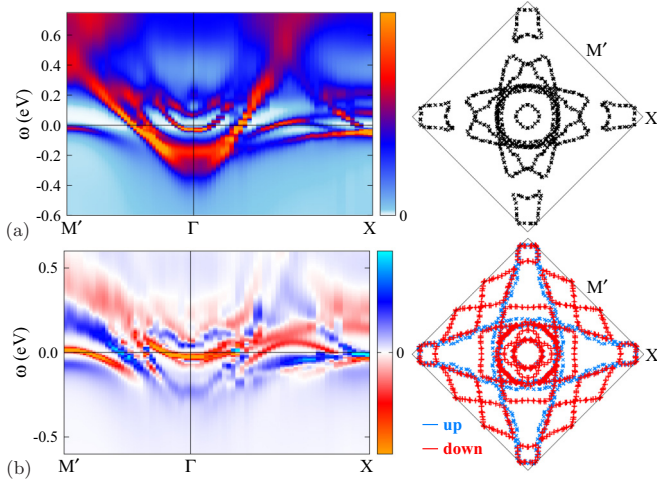


FIG. 5. (Color online) k -resolved DFT+DMFT spectral data for VH-LAO/STO. (a) PM case: $A(\mathbf{k}, \omega)$ (left), Fermi surface (right). (b) FM case: Spectral spin contrast $A_{\uparrow}(\mathbf{k}, \omega) - A_{\downarrow}(\mathbf{k}, \omega)$ (left), spin-resolved Fermi surface (right).

(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. 4(a) reveals a shallow lower Hubbard band. This incoherent excitation is dominantly from the e_g -like state, as verified by the $\text{Ti}^{(1)}$ impurity spectral function [cf. Fig. 4(b)]. The \tilde{e}_g peak position at ~ -1.2 eV is in excellent agreement with photoemission data [19,20]. A QP peak in favor of xy but additional \tilde{e}_g weight completes the itinerancy/localization dichotomy originating within the $\text{Ti}^{(12)}\text{O}_2$ layer. Orbital-based differences in the interface effective-mass are noted by $1/Z_{xy} = m^*(xy)/m_{\text{LDA}}(xy) \sim 1.3$, in good accordance with Shubnikov–de Haas measurements [48], and $1/Z_{\tilde{e}_g} = m^*(\tilde{e}_g)/m_{\text{LDA}}(\tilde{e}_g) \sim 2.1$. Mass renormalization for $\text{Ti}^{(345)}$ t_{2g} -like states is rather weak. From Table I, a single electron is associated with each $\text{Ti}^{(12)}$ ion in the VH case. Roughly 3/4 thereof are of stronger-localized \tilde{e}_g and 1/4 of stronger-itinerant xy character. Significant charge disproportionation between $\text{Ti}^{(1)}$ and $\text{Ti}^{(2)}$ is not observed. The spectral function $A(\mathbf{k}, \omega)$ in Fig. 5(a) reveals DMFT self-energy-induced shifts of spectral weight (see the Appendix) compared to the LDA bands [Fig. 2(c)]. A flattened xy -like QP band starts right below the Fermi level at Γ . That shifted low-filled xy -like QP band carries also $\text{Ti}^{(5)}$ weight, i.e., away from the direct interface. Therefore lowest-energy QP bands around Γ are not only associated with interface-nearest ($\text{Ti}^{(12)}$) electrons. The hybridized \tilde{e}_g/xy band close to M' rests just below ε_F , and the \tilde{e}_g - and xz/yz -like bands along Γ - X are now partly merged. The PM Fermi surface (FS) shown in Fig. 5(b) displays the experimentally detected [20] fourfold starlike shape extending towards X .

Albeit numerically demanding, no stable ferromagnetism is deduced for the DF structure within DFT+DMFT. Allowing for FM spin polarization in the VH case leads to magnetic order, nearly exclusively located in the $\text{Ti}^{(12)}\text{O}_2$ layer (cf. Table I). The FM phase is energetically indeed weakly favored

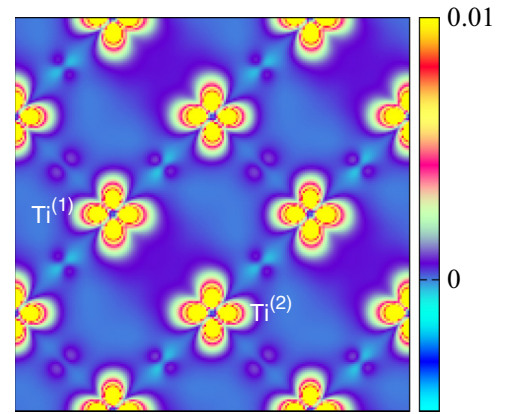


FIG. 6. (Color online) DFT+DMFT real-space spin contrast $\rho_{\uparrow} - \rho_{\downarrow}$ in the correlated charge density within $\text{Ti}^{(12)}\text{O}_2$ interface layer for the ferromagnetic phase of the VH structure.

against the PM phase with $\Delta E \sim 10$ meV/ $\text{Ti}^{(12)}$. A local $\text{Ti}^{(12)}$ moment of $\sim 0.09\mu_B$ is detected, in excellent agreement with experiment [13]. Notably this moment builds up from polarizing both minimal $\text{Ti}^{(12)}$ orbitals, yet surprisingly xy , though lower filled, has a larger share. Figure 6 displays that the real-space spin polarization within the FM phase of the VH structure is indeed largest for the xy states. At ε_F , electrons are either of \tilde{e}_g spin-down or close to spin-average t_{2g} (only $\text{Ti}^{(12)}$ xy contribution shown) flavor [see Fig. 4(b)]. Thus the FM state in LAO/STO has a truly intriguing itinerancy, emerging from many-body scattering between QPs and nearly localized electrons. The spectral spin contrast in Fig. 5(b) shows that major spin polarization is tied to low energy. Correlation-induced exchange splitting leads to a modified fermiology, especially close to M' , where a spin-down QP band with substantial \tilde{e}_g weight finally forms a hole pocket. While the spin-up FS keeps the starlike shape, the spin-down FS extends now also towards the neighborhood of M' , covering the full BZ.

Since the PM spectral intensity at ε_F is enhanced with correlations, the Stoner criterion rewritten for the Hubbard model as $UA(\varepsilon_F) > 1$ would be 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 [49,50]. Especially here due to the vacancy-induced minimal scenario of a nearly half-filled \tilde{e}_g orbital and a weakly filled xy orbital, J_H -driven double-exchange (DE) processes dominantly account for FM order [51,52]. However a distinct orbital-character separation into localized spin and itinerant electrons as in the standard DE model Hamiltonian is not fully adequate. Figure 7(a) displays the temperature dependence of the PM $\text{Ti}^{(1)}$ self-energy part $\text{Im} \Sigma(i\omega_n)$ for Matsubara frequencies $\omega_n = (2n+1)\pi T$. Besides showing the noted orbital differentiation in the QP renormalization $Z = (1 - \frac{\partial \text{Im} \Sigma(i\omega)}{\partial \omega} |_{\omega \rightarrow 0^+})^{-1}$ it reveals insight into the electron-electron scattering [$\sim -Z \text{Im} \Sigma(i0^+)$] for \tilde{e}_g, xy .

The more localized \tilde{e}_g electrons are less coherent at higher T than the xy ones, because of an increased $-\text{Im} \Sigma(i0^+)$. Consistent with a DE-like mechanism the coherency in the FM phase at low temperature is higher than in the PM phase

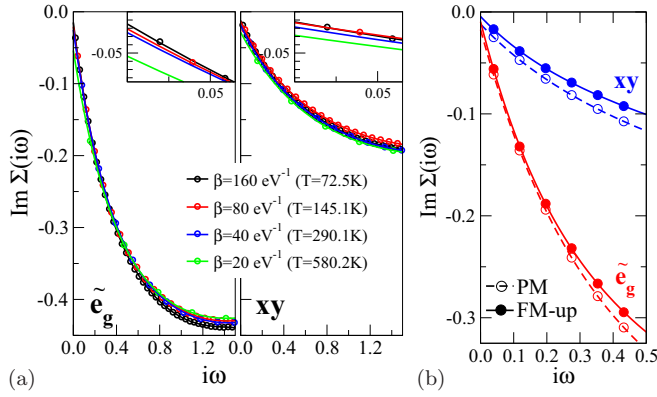


FIG. 7. (Color online) $\text{Im } \Sigma(i\omega_n)$ of $\text{Ti}^{(1)}$ impurity self-energy in VH case. Lines are from fifth-order polynomial interpolation in a larger frequency range. (a) PM data at various T (insets: blow-up close to zero frequency). (b) Data at $T = 145.1$ K.

[see Fig. 7(b)]. 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 using the spin-averaged charge density in the DFT part we encounter significantly reduced $\text{Ti}^{(12)}$ moments $\sim 0.01\mu_B$ at $T = 290$ K. In line with experimental findings [12], the Curie temperature of ferromagnetic LAO/STO may thus be estimated to lie somewhat above room temperature.

VI. CONCLUSIONS

Realistic many-body theory for the LAO/STO interface identifies the essential ingredients for metallic ferromagnetism and characterizes the underlying electronic state. Correlations from local Coulomb interactions in the DF interface are not strong enough within DFT+DMFT to cause an FM state or straightforward charge-ordering instabilities. Ferromagnetism only appears with oxygen vacancies *and* electronic correlations. Note that pure *static* correlation effects based on DFT+ U also yield FM moments in the VH case [29], but too large in 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].

The basic many-body behavior is understood within a minimal two-orbital \tilde{e}_g - xy picture originating in the nearest-interface TiO_2 layer, derived from the full supercell electronic structure. Strongly renormalized temperature-dependent QPs as well as significant incoherent spectral weight are revealed. In fact the -1.2 eV peak known from photoemission can be readily identified as an \tilde{e}_g -like lower Hubbard band. Double-exchange processes between more localized \tilde{e}_g and more itinerant xy lead to ferromagnetism. The intricate fermiology of especially the FM state involves at least two (\tilde{e}_g , xy) carrier types. Details on charge transfers, orbital contributions, etc., still ask for an inclusion of Ti states from more distant TiO_2 layers. Although we here studied two extreme structural cases, i.e., stoichiometric and with high vacancy concentration, the qualitative electronic aspects due to oxygen vacancies are believed to hold also for more demanding diluted scenarios. In this regard, multicomponent cluster-expansion based approaches [53] provide a route to access the generic thermodynamics of vacancies and other possible defects [54] at the LAO/STO interface. Further theoretical work on the correlated electronic structure is needed to address the magnetic anisotropy and the connection/coexistence of ferromagnetism with superconductivity. Finally, time-dependent manipulation of the intricate electronic states at the interface via pump-probe techniques may lead to fascinating new nonequilibrium physics.

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APPENDIX: 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 30×30 for the DF calculation and 20×20 for the VH one. For instance, the in-plane nearest-neighbor (NN) $\text{Ti}^{(12)}$ Hamiltonian block in the latter case reads

$$H_{\tilde{e}_g, xy}^{(\text{KS}, 12, \text{NN})} = \begin{pmatrix} \text{Ti}^{(1)} & & & & & & & & & \\ & \text{Ti}^{(1)} & & & & & & & & \\ & & \text{Ti}^{(2)} & & & & & & & \\ & & & \text{Ti}^{(2)} & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \end{pmatrix}, \quad (\text{A1})$$

whereby each on-site Ti subblock consists of a 2×2 matrix for \tilde{e}_g and xy 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 Δ_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 ε_{CSC} is the converged local

level energy from the KS-like part within DFT+DMFT, Δ_{DC} is the orbital-independent but site-dependent shift from the fully localized double counting, and ε_{KS} is 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.

TABLE II. Kohn-Sham levels and correlation-induced shifting Δ_c (in meV) for (left) $\tilde{e}_g/(xz/yz)$ and (right) xy at $\text{Ti}^{(12)}/\text{Ti}^{(345)}$, in the VH structure within DFT+DMFT at $T = 145.1$ K.

| | $\text{Ti}^{(1)}$ | $\text{Ti}^{(2)}$ | $\text{Ti}^{(3)}$ | $\text{Ti}^{(4)}$ | $\text{Ti}^{(5)}$ |
|---------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| ε_{KS} | 416 729 | 397 728 | 865 1016 | 903 1016 | 870 1086 |
| Δ_c | 244 160 | 249 146 | 191 240 | 200 250 | 279 372 |

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