Towards Mott design by $\delta$-doping of strongly correlated titanates

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Abstract
Doping the distorted-perovskite Mott insulators LaTiO$_3$ and GdTiO$_3$ with a single SrO layer along the [001] direction gives rise to a rich correlated electronic structure. A realistic superlattice study by means of the charge self-consistent combination of density functional theory with dynamical mean-field theory reveals layer- and temperature-dependent multi-orbital metal-insulator transitions. An orbital-selective metallic layer at the interface dissolves via an orbital-polarized doped-Mott state into an orbital-ordered insulating regime beyond the two conducting TiO$_2$ layers. We find large differences in the scattering behavior within the latter. Breaking the spin symmetry in $\delta$-doped GdTiO$_3$ results in blocks of ferromagnetic itinerant and ferromagnetic Mott-insulating layers that are coupled antiferromagnetically.

1. Introduction
In view of future technological applications, the investigation of oxide heterostructures provides the possibility for exploring novel composite materials beyond nature’s original conception (see, e.g., [1–3]) for reviews). Additionally, this research extends the concept of materials design towards the realm of strongly correlated systems. Many of the essential heterostructure building blocks either harbor partially filled transition-metal $d$-shells already in their bulk configuration (e.g., LaTiO$_3$, LaVO$_3$, GdTiO$_3$, etc) or display such partial filling due to interface doping (e.g., for SrTiO$_3$). Therefore, weakly screened Coulomb interactions may give rise to explicit many-body effects that eventually govern the materials physics. Unusual metallicity from combining bulk band insulators, emergent magnetic order, superconductivity, or large thermopower are only a few fascinating phenomena that occur in the interfacing regions. Engineering such structured matter allows for a direct manipulation of systems in or close to the Mott-critical regime, i.e., offers the potential for Mott design. A specific realization thereof, the $\delta$-doped oxide heterostructures [4–7] (i.e., introducing well-defined impurity monolayers into a given host oxide compound) recently emerged as a canonical method to create challenging electronic states from experimental fabrication. Especially, the $\delta$-doping of Mott insulators [8–11] not only has relevance in the designing context, but furthermore sheds light on the generic physics of the realistic doped-Mott state in a controlled way without the usual complications arising from disorder and other features of random impurity doping.

In this work we use a first-principles many-body approach to investigate the $\delta$-doping of the Mott insulators LaTiO$_3$ (LTO) and GdTiO$_3$ (GTO). The bulk materials are examples of two qualitatively different trends within the series of perovskite-like $R$TiO$_3$ compounds ($R =$ rare-Earth element) [12] with GdFeO$_3$-type distortion. While for a smaller rare-Earth ionic radius (Yb, Y, Gd) the systems become ferromagnetic (FM) at low temperature, for a larger radius (Sm, Nd, La) the materials are G-type antiferromagnetic (AFM) in the crystallographic $a$ direction upon cooling. For GTO the Curie temperature is 36 K, and the Néel temperature of LTO amounts to 146 K. An increasing deviation of the Ti-O-Ti bond angle from 180° from La to Y is key to the change of magnetic ground state among the titanates [13–17]. The crucial low-energy electron states are dominated by the threefold of Ti($t_{2g}$) orbitals, with a nominal filling of one electron. Numerous theoretical studies are devoted to reveal the electronic structure of these bulk Mott insulators [18–24]. Especially, the very detailed ab-inito study of Pavarini et al [23] covers many aspects of the representants LaTiO$_3$ and YTiO$_3$, from
the generic band structure to crystal-field tight-binding considerations, up to the inclusion of correlation effects.

The latter are shown to be important in driving significant orbital ordering in these $3d^4$ materials, which renders other orbital-degenerate modelings questionable.

The main intention here is to shed light on the correlation physics of $\delta$-doped heterostructures as well as to promote the RTiO$_3$ physics to the next level by investigating the behavior from doping with a single SrO layer. We thereby concentrate on the temperature regimes above the bulk magnetic ordering. Two main question arise in the latter scenario: the first one concerns the appearance of metallization via the non-random hole doping, and if it sets in, the characterization in terms of the multi-orbital Ti manifold and its layer dependence. When a (layer-dependent) Mott state is reached, its possible deviation from the known bulk Mott-insulating state is secondly of key interest. The clarification of the correlated electronic structure in this canonical structure case is highly relevant for the understanding of other layerings and possible applications, e.g., in the area of solar cells [25].

Using the charge self-consistent combination of density functional theory (DFT) with dynamical mean-field theory (DMFT) in a superlattice architecture, we indeed reveal a very rich electronic-structure phenomenology. Layer-dependent multi-orbital metal-insulator transitions via $\delta$-doping are identified for the case of SrO/LTO and SrO/GTO heterostructures that involve three different electronic regimes. With increasing distance to the doping layer, an $xy$-dominated metallic state settling right at the interface is replaced by an orbital-polarized doped-Mott metallic layer that transforms to bulk-modified insulating Mott layers. Embedding such complex electron states within oxide heterostructures opens the door for many ways of manipulations and can lead to the identification of building blocks for new devices.

2. Theoretical framework

On the level of the local density approximation (LDA) to DFT, a mixed-basis pseudopotential framework [26, 27] is applied for the structural optimization of the $\delta$-doped supercells and the basic electronic structure investigation. Norm-conserving pseudopotentials as well as a combined basis of plane waves and localized functions for Ti ($3d$) and O ($2s2p$) are utilized. The latter allow for a moderate plane-wave cutoff energy $E_{\text{cut}} = 13\text{Ryd}$ for the demanding supercell calculations, which are based on a $5 \times 5 \times 3$ k-point mesh in reciprocal space. Though $f$-electrons can also be treated also in many-body bulk computations, we here aim for novel correlation effects dominantly from first-principles $3d$ electrons in challenging heterostructure architectures. Thus effects of possible $4f^2$ states are captured approximately. In La those states are unoccupied in the atom and form empty conduction states in LTO. One may neglect them for the present purpose to a good approximation in the pseudopotential construction and the localized-function basis. Contrary to the neighboring band-insulating EuTiO$_3$ compound with Eu$^{2+}$ and Ti$^{4+}$, GTO harbors Gd$^{3+}$ and Ti$^{3+}$. This shifts the half-filled $4f$ shell (occupation seven electrons) of Gd further down in energy, and with an assumed large intra-orbital Coulomb interaction, this local mainfold, deep in energy, has no quasiparticle contribution at low energy. Hence the Gd ($4f$) shell is not of eminent importance in GdTIO$_3$ and is here put in the pseudopotential frozen core.

Full local electronic correlation effects beyond the static (i.e., LDA, LDA+U) realm are taken care of by the DMFT within the framework of charge self-consistent DFT+DMFT [28–30]. The multi-site and -orbital correlated subspace where explicit Coulomb interactions are treated on the many-body level is here defined by the $t_{2g}$-like low-energy crystal-field (cf) bases of the various Ti ions in the given structures. It is obtained by tailored projected local orbitals [31–33] based on a set of low-energy Kohn–Sham (KS) states. The orbital projections are given by linear combinations of the original ($xz$, $yz$, $xy$) functions that diagonalize the local $t_{2g}$-like $3 \times 3$ orbital density matrix on each Ti ion, respectively. In the case of the bulk compounds, the 12 low-energy KS bands close to the Fermi level are used to facilitate the projection. All Ti ions are equivalent by symmetry in the bulk GdFeO$_3$ structure, and the site-dependent projections can be chosen such that a single $3 \times 3$ self-energy matrix $\Sigma$ ($\omega$) is converged. For the $\delta$-doped compounds, a multi-site DFT+DMFT scheme is put into practice with five inequivalent Ti ions in the chosen supercells (see sections 3 and 5). There a KS manifold of 60 low-energy bands enters the projection.

A rotational-invariant three-orbital Hubbard Hamiltonian in Slater–Kanamori parameterization is applied on each Ti site. The intra-orbital Coulomb interaction is chosen as $U = 5$ eV and the Hund’s exchange as $J_\text{H} = 0.64$ eV, identical to former LDA+DMFT studies of bulk titanates [21, 23]. Continuous-time quantum Monte Carlo in the hybridization expansion [34–37] is utilized to solve the DMFT impurity problems. At each correlated Ti site $i$ and orbital $m$, a double-counting (DC) correction of the fully-localized form [38] making use of the local particle-number operator $n_i$ (i.e., $\Sigma^\text{DC} = U \left( \langle n_i \rangle - 1/2 \right) - J_\text{H} \left( \langle n_m \rangle - 1/2 \right)$ with $\sigma = 1, \downarrow$) is applied to the self-energy in the complete charge self-consistent convergence cycle. The resulting local and total spectral functions are derived from analytical continuation of the Green’s functions in Matsubara space via the maximum-entropy method.
Note that different or larger correlated subspaces, e.g., by including \( \text{O}(2p) \)-dominated KS band states in the projection, are possible and currently under investigation for oxide bulk Mott insulators \([39, 40]\). But since our focus is on the challenging large-scale heterostructure problem, where such recent extensions are very expensive, we work in a minimal \( t_{2g} \)-based correlation framework. In an initial study \([10]\), the \( \delta \)-doping of LTO with a single SrO layer was in part already investigated within DFT+DMFT. But there the inplane lattice constant \( a = b \) of bulk SrTiO\(_3\), a site-averaged DC as well as cubic \( t_{2g} \) projections (i.e., not adapted to the local cf eigenbasis) were used. Albeit valuable insight was obtained, the correlation physics of such heterostructures is rather sensitive to details, and therefore we here advance in the modelling. Concerning the notorious DC term, a site-dependent DC correction is more tailored to the real-space problem of correlated sites with different distances to existing interfaces.

3. Crystal-structure considerations

Bulk crystal structures of LTO and GTO with \( Pbnm \) space group are experimentally well studied, and we here utilize available x-ray diffraction data \([12]\) (see figure 1(a)). Relevant parameters of the distorted perovskite structure with four formula units in the primitive cell are tilt and in-plane rotation of the \( \text{TiO}_6 \) octahedra, both with respect to the \( c \)-axis. The deviations from the perovskite structure are larger in GTO. A measure thereof is given by the angles between \( \text{Ti-O}_1-\text{Ti} \) and \( \text{Ti-O}_2-\text{Ti} \), where \( \text{O}_1 \) marks the apical oxygen ion and \( \text{O}_2 \) the one in the basal plane of the octahedron. The latter plane is furthermore distorted differently in both structures. While in LTO that distortion is rectangular, in GTO it is of parallelogram shaping \([12]\).

To facilitate the \( \delta \)-doping scenario, a single SrO layer is inserted in the hosting titanates within a periodic superlattice architecture in the [001] direction, respectively. Along the \( c \)-axis the supercells (see figure 1(b)) consist of 10 \( \text{TiO}_2 \) and 9 \( \text{La(Gd)} \)O host layers in between the SrO monolayers. This amounts to a separating distance of about 4 nm between the latter. A \( \sqrt{2} \times \sqrt{2} \) unit is chosen in lateral in-plane direction to allow for the \( \text{TiO}_6 \) octahedral tilts/rotations and distortions, i.e., each \( \text{TiO}_2 \) layer includes two \( \text{Ti} \) sites. Thus there are 20 \( \text{Ti} \) ions in these supercells with a total number of 100 atoms. For the lattice parameters \( a, b, \) and \( c \) the experimental bulk LTO/GTO values are used, and the atomic positions are obtained from minimizing the atomic forces within LDA down to 10 mRyd/a.u. per site. Note that the method of choice for structural optimization in low-symmetry correlated materials, i.e., LDA, GGA, or static DFT+U \([41]\), is still open and a matter of debate.

It is well known that the tilts, rotations, and distortions of the \( \text{TiO}_6 \) octahedra in the \( \text{RTiO}_3 \) series are crucial for the Mott insulating as well as the magnetic state. Thus the changes thereto by the SrO doping layer may have a strong influence on the resulting electronic structure. The relaxed structural data is summarized by providing layer-dependent bond angles and bond lengths (see figure 2). In general, the LDA bond angles in the \( \delta \)-doped
structures turn out somewhat larger than the experimental values for the bulk stoichiometric systems. But the hierarchy, marking GTO with stronger tilts and rotations of the TiO\textsubscript{6} octahedra, remains intact. For both structures, the differences in tilts and rotations are strongest close to the SrO doping layer. The octahedral tilt and rotation are related to the Ti-O\textsubscript{1}-Ti, Ti-O\textsubscript{2}-Ti angles. The former (latter) angle is somewhat enhanced (reduced) close to the interface in the LTO case. In the GTO case both angles are shifting in the direction of the non-distorted value of 180° when approaching the interface. Note that these overall smaller tilts compared to the bulk cases are in qualitative agreement with recent measurements using scanning transmission electron microscopy on SrO quantum wells in GTO [42]. The LDA bond lengths between the O\textsubscript{2} ions in the octahedral basal plane are in general somewhat lower than in the experimental bulk structures. Close to the interface the rectangular distortion is enhanced in the LTO case, while for δ-doped GTO some shrinking of the basal plane may be noticed.

Our structural data is in line with recent GGA+U calculations by Chen et al, where a smaller supercell for δ-doped GTO along the [001] direction was used. On the experimental side, Zhang et al [8, 42, 43] studied the structural modifications due to doping GTO with a SrO monolayer, but using a different interface geometry. There it is defined by the directions [110] and [001] i.e., the c-axis parallel to the interface and a, b inclined, whereas in the present work the interface is given by the directions [100] and [010]. The observation of somewhat smaller octahedral tilts right at the interface agrees between theory and experiment. Still the geometry influence on the electronic structure may be significant, e.g., because of orbital-ordered Mott(-like) states with a unique directional character.

4. Electron states in bulk LaTiO\textsubscript{3} and bulk GdTiO\textsubscript{3}

This section summarizes the electronic structure of the bulk compounds to set the stage for comparison with the δ-doped cases. The La- and Gd-titanate are well-defined metals in the conventional KS representation of DFT. Both display an \textit{t}_{2g}^-\textit{e}_{g}^-\textit{t}_{2g}^-\textit{e}_{g}^-\textit{t}_{2g}^-\textit{e}_{g}^- low-energy manifold close to the Fermi level \(\varepsilon_F\) in LDA (see figure 3) of bandwidths \(W_{\text{LTO}} = 1.9\) eV and \(W_{\text{GTO}} = 1.8\) eV. The GTO density of states (DOS) at \(\varepsilon_F\) is larger than the LTO one, and the \textit{t}_{2g}^-\textit{e}_{g}^- gap in the unoccupied energy region is also increased for the former. Therefrom the Gd compound is somewhat more susceptible to correlation effects than the La one.

The LTO local crystal-field basis from the projected local orbitals reads (note that phases differ on the various Ti sites)

\[
\begin{pmatrix}
1 \\ 2 \\ 3 \\
\end{pmatrix} = \begin{pmatrix}
0.710 & 0.274 & -0.648 \\
0.262 & 0.752 & 0.605 \\
0.653 & -0.600 & 0.462 \\
\end{pmatrix} \begin{pmatrix}
xz \\ yz \\ xy \\
\end{pmatrix}
\]

with level energies \(\varepsilon_{cl}^{(1)} = 483\) meV, \(\varepsilon_{cl}^{(2)} = 379\) meV, and \(\varepsilon_{cl}^{(3)} = 491\) meV. Lowest in energy is state \(2\), with dominant \(yz\) and weakest \(xz\) contribution, in qualitative agreement with the previous study [23] based on linear/Nth-order muffin-tin orbital methods in the atomic-sphere approximation. Crystal-field splittings \(\Delta_{1,3} = \).
$\varepsilon_{cf}^{(1)}$ of the order of 100 meV turn out to be somewhat smaller in the present work. The local DOS of these states is plotted in figure 3 and shows no very significant orbital discrimination in its shape. No sizable orbital polarization is seen on the LDA level; the single Ti ($3d$) electron is shared among the adapted states.

For GTO the corresponding local cf basis is given by

\[
\begin{pmatrix}
|1\rangle \\
|2\rangle \\
|3\rangle
\end{pmatrix} =
\begin{pmatrix}
0.639 & 0.449 & 0.625 \\
0.707 & -0.664 & -0.245 \\
-0.305 & -0.598 & 0.741
\end{pmatrix}
\begin{pmatrix}
xz \\
yz \\
xy
\end{pmatrix},
\]

with level energies $\varepsilon_{cf}^{(1)} = 319$ meV, $\varepsilon_{cf}^{(2)} = 483$ meV, and $\varepsilon_{cf}^{(3)} = 456$ meV. State $|1\rangle$ with lowest energy is here a more balanced combination of the original $t_{2g}$ orbitals, with the weakest contribution from $yz$. The cf splittings are similar to the LTO case, with a small increase in numbers. Stronger orbital discrimination is visible on the LDA level; i.e., the local DOS of the $|1\rangle$ state marks not only a smaller bandwidth but has a significantly larger value at the Fermi level. This leads to some orbital polarization towards $|1\rangle$ in the single-electron share.

Figure 4 shows the obtained effective $t_{2g}$ orbitals for both titanates. As within other downfolding schemes applied to transition-metal oxides [23, 44], the Wannier-like functions exhibit significant weight on the nearby oxygen ions, as expected via the projection from low-energy KS states. Note that though the projection orbitals are atomic-like functions [32], the resulting correlated subspace is composed of Wannier-like functions due to the projection onto selected KS states. Concerning the lowest-energy cf orbitals, the $|2\rangle$ state of LTO is mainly oriented along the $b$-axis, while the $|1\rangle$ state of GTO is aligned along the $a$-axis. Furthermore, the GTO $|3\rangle$ orbital has a clearer in-plane $xy$ character, whereas a clear resemblance thereof is lacking in LTO.

The electronic structure of these compounds is modified substantially within DFT+DMFT. For both materials the experimental room-temperature Mott-insulating state is confirmed (see figure 3). Lower Hubbard bands are located at $\sim 1.2$ eV for LTO and at $\sim 1$ eV for GTO. In our present scheme the charge gaps amount to $\Delta_\text{LTO}^b \sim 0.5$ eV and $\Delta_\text{GTO}^b \sim 0.8$ eV. While the latter value is in good agreement with experimental data of about $0.75$ eV [45], our result for the LTO value is larger than $\Delta_\text{LTO} \sim 0.2 \sim 0.3$ eV from experiment [46, 47]. A smaller theoretical charge gap was obtained in previous non-charge-self-consistent studies [21], with a similar correlated subspace and the same interaction parameters, but at a much higher temperature $T = 1200$ K. Recent DFT+DMFT with a larger correlated subspace and including the unoccupied $4f$ state reaches a smaller value also close to room temperature [39]. Substantial orbital polarization takes place in the Mott state, with dominant filling of the effective $|2\rangle$ ($|1\rangle$) orbital in LTO (GTO). The occupation numbers for $|1\rangle$, $|2\rangle$, $|3\rangle$ read (0.22, 0.59, 0.19) for LTO and (0.66, 0.18, 0.16) for GTO. Hence, with correlations, close to 2/3 of the single $t_{2g}$ electron resides in the lowest cf level.

Figure 3. Spectral-function comparison between LDA and DFT+DMFT ($T = 290$ K) for the bulk case of (a) LTO and (b) GTO. Top: total spectrum; bottom: local orbital-resolved spectrum with dashed lines for the LDA result.

New J. Phys. 17 (2015) 043026 F Lechermann and M Obermeyer
5. Electron states in $\delta$-doped compounds without broken spin/charge symmetry

Realistic correlation effects from $\delta$-doping LTO and GTO are approached in a multi-site DFT+DMFT scheme. The five inequivalent Ti ions in the supercell structures allow for corresponding layer-dependent effective $t_{2g}$ DMFT self-energies $\Sigma$ 1–5 beyond static considerations. In this section we first concentrate on the electronic structure without possible breaking of spin and charge symmetries, i.e., paramagnetic states as well as charge-balanced solutions. To this, no intra-layer discrimination of both Ti ions per layer is performed, respectively. Symmetry-broken solutions for $\delta$-doped GTO will be discussed in section 6.

Table 1 provides the list of matrices, based on LDA calculations, transforming the original ($xz$, $yz$, $xy$) orbitals into the now layer-dependent, cf bases ($\vert 1 \rangle$, $\vert 2 \rangle$, $\vert 3 \rangle$). The variations in the coefficients are largest between the groups (Ti1,Ti2) and (Ti3,Ti4,Ti5), but the classification of the effective orbitals remains stable across the different TiO$_2$ layers. From the onsite level energies $\varepsilon_{cf}$ of the effective cf states it is seen that again the $\vert 2 \rangle (\vert 1 \rangle)$ state is lowest on the Ti3–5 sites in the doped LTO (GTO) case, as found for the bulk Ti site. The level spacing on those three sites is also nearly identical to the bulk for GTO, whereas for the LTO case the energy difference is up to 60% larger. On Ti2 the level energies come already substantially closer compared to Ti3–5.

Qualitative energetic changes occur for the TiO$_2$ layer closest to the SrO doping layer: the Ti1 site has state $\vert 3 \rangle$, with dominant $xy$ contribution, lowest for both titanate types. The single SrO layer induces hole doping in the 3$d^1$ titanates, trying to shift the nominal Ti$^{3+}$ state towards Ti$^{4+}$, as found in bulk SrTiO$_3$. Since the complete unit cell hosts 10 TiO$_2$ layers, the doping amounts to 0.1 electrons per Ti ion. Figure 5 displays the resulting bond charge density (BCD) within LDA and DFT+DMFT. These densities are evaluated as differences between the obtained total charge density and the original overlaid atomic charge densities, thus revealing the key effects due to crystallization. One main BCD feature for the considered transition-metal-oxide compounds is the ionic charge transfer from titanium to oxygen. Beyond that the LDA BCD does not show many more deeper characteristics. The BCD from DFT+DMFT, on the other hand, clearly reveals the orbital polarization in the different crystallographic directions for LTO and GTO far from the SrO layer. A difference plot visualizes this polarization readily as local correlation effects, i.e., onsite 3$d$ charge transfers. Especially in the GTO case, a further correlation-induced charge transfer to oxygen ions occurs. Close to the SrO layer the orbital polarization is weak; mainly, a minor additional charge transfer into that region from the interior within DFT+DMFT compared to LDA becomes visible.

Further details on the $\delta$-doped LTO correlated electronic structure are revealed from the $k$-summed one-particle spectral function $A(\omega) = \sum_k A(k, \omega)$. The studied $T$ range starts above 1000 K and ends at 145 K, close to the bulk Neél temperature. The total spectrum has a metallic character for all investigated temperatures but exhibits a strong transfer of spectral weight to Hubbard peaks (see figure 6(a)). Compared to the bulk case, the center of the lower Hubbard peak is shifted upwards to ∼0.9–1 eV. The quasiparticle (QP) peaks have significant

![Figure 4. Crystal-field orbitals from the projection formalism for the bulk cases of LTO (top) and GTO (bottom). La (blue), Gd (violet), Ti (gray), O (red).](image-url)
is the orbital-independent but site-dependent shift from the fully localized DC, and is the local level energy from the KS-like part in DFT.

Also seen in the local Ti-resolved below 100 K. In general, the temperature dependence is more delicate in orbital-balanced character but clearly favoring the ordering of bulk GTO is well below 100 K, we shifted the temperature range and set distinct regimes (see also

Table 1. Layer-dependent Ti cf bases within the projected local orbitals, defining the correlated subspace for the δ-doped compounds. The given 3 × 3 matrices transform the (xz, yz, xy) orbitals to the tailored (1), (2), (3) orbitals in the same manner as given in equations (1) and (2) for the respective bulk case. The quantities εcf denote the respective onsite level energies (in meV) for the resulting tailored orbitals.

|      | δ-LTO       | δ-GTO       |
|------|-------------|-------------|
|      | xz  | yz  | xy  | εcf | xz  | yz  | xy  | εcf |
| Ti1  | [1] | -0.930 | 0.212 | -0.300 | 656 | -0.735 | 0.227 | -0.638 | 668 |
|      | [2] | -0.354 | -0.739 | 0.573 | 663 | -0.328 | -0.944 | 0.041 | 730 |
|      | [3] | 0.100 | -0.639 | -0.763 | 597 | 0.593 | -0.240 | -0.769 | 577 |
| Ti2  | [1] | 0.943 | 0.322 | 0.086 | 569 | 0.746 | -0.268 | 0.609 | 409 |
|      | [2] | -0.176 | 0.699 | -0.693 | 428 | 0.362 | 0.932 | -0.032 | 534 |
|      | [3] | -0.284 | 0.638 | 0.716 | 587 | -0.559 | 0.245 | 0.792 | 508 |
| Ti3  | [1] | -0.984 | 0.168 | 0.056 | 545 | 0.718 | 0.321 | 0.617 | 387 |
|      | [2] | -0.165 | -0.754 | -0.636 | 387 | 0.324 | -0.939 | 0.111 | 524 |
|      | [3] | -0.065 | -0.635 | 0.770 | 577 | 0.616 | 0.120 | -0.779 | 502 |
| Ti4  | [1] | -0.982 | 0.190 | 0.002 | 544 | -0.715 | -0.331 | 0.616 | 382 |
|      | [2] | -0.146 | -0.759 | 0.634 | 390 | -0.289 | 0.942 | 0.170 | 519 |
|      | [3] | 0.122 | 0.622 | 0.773 | 578 | -0.637 | -0.057 | -0.769 | 498 |
| Ti5  | [1] | -0.978 | 0.210 | 0.012 | 547 | 0.721 | 0.325 | 0.612 | 384 |
|      | [2] | -0.171 | -0.758 | -0.629 | 395 | 0.305 | -0.942 | 0.140 | 521 |
|      | [3] | -0.123 | -0.617 | 0.777 | 575 | 0.622 | 0.086 | -0.779 | 499 |

T dependence, displaying bad-metal behavior at elevated temperatures. Only well below room temperature a clear resonance occurs at the Fermi level. A layer-dependent multi-orbital Mott transition is inferred from the local Ti-resolved A(ω). Its structure renders it possible to separate the δ-doped electronic structure into three distinct regimes (see figure 6(b)): far from the doping layer the material is in an orbital-ordered Mott state (I), with insulating layers derived from Ti3−5. Notably, these Mott layers are still different from the bulk-LTO state. The orbital polarization towards (layer-dependent) (2) is nearly complete, already close to room temperature (see also figure 6(c)), while in bulk LTO only about 2/3 of the single electron resides in state (2). This is in line with the finding of a stronger energy separation of the onsite cf levels in δ-LTO (see table 1). In addition, the local gap charge is somewhat reduced compared to the bulk value. For higher T the gaps are partially filled by incoherent excitations. The second regime (II) is built from the next-nearest TiO2 layer from the interface, an orbital-polarized doped-Mott layer with QPs at low energy. While the occupied part, including Hubbard and QP excitation, is dominated by (2), minor QP weight is shifted towards (1), (3). Finally, the third regime (III) is formed by the nearest TiO2 layer right below SrO, an orbital-selective metallic film with comparatively more orbital-balanced character but clearly favoring the xy-dominated (3) state in the occupied part. The coherence of the QPs therein increases significantly at low T, while the orbital fillings are rather temperature independent. About 0.6 electrons are located at Ti1. The remaining holes are mostly at Ti2, but the hole doping is not fully perfect; i.e., some holes seem to remain within the SrO layer.

Accordingly, the spectral data for δ-doped GTO is exhibited in figure 7. Since the Curie temperature for FM ordering of bulk GTO is well below 100 K, we shifted the temperature range and set T = 73 K as the lowest value. In comparison to δ-LTO, the QP coherence close to the Fermi level is enlarged but shows a surprising decline below 100 K. In general, the temperature dependence is more delicate in δ-doped gadolinium titanate, as can be also seen in the local Ti-resolved A(ω). The three encountered electronic regimes are also present here, now with the corresponding state (I) as the Mott-dominating one. But for Ti3 and Ti4 there is in addition a T-dependent transition between regimes I and II. Furthermore, the gapped QP of (3) in the occupied region has a much stronger signature and resides just below the Fermi level. The orbital-occupation character far away from the interface resembles the LTO case, here strongly polarized in the (1) state with clear 3d4 total filling. Again the strength of orbital polarization is significantly increased, compared to the GTO bulk case. Note that here, since the LDA onsite level differences are similar to the bulk, the DMFT self-energy is nearly exclusively responsible for that increase. In general the correlation-induced local level shift renormalizing the original cf splitting is given by $\Delta \varepsilon = \varepsilon_{\text{SCS}} + \text{Re } \Sigma (\text{i}0^+) - \Delta_{\text{DC}} - \varepsilon_{\text{cf}}$. Here $\varepsilon_{\text{SCS}}$ is the local level energy from the KS-like part in DFT+DMFT, $\Delta_{\text{DC}}$ is the orbital-independent but site-dependent shift from the fully localized DC, and $\varepsilon_{\text{cf}}$ is the original cf level energy from LDA. In the close-to-interface regimes II and III there are slight differences, namely, marginal depletion of the doped-Mott state at lower T in II and somewhat stronger orbital discrimination in III.
The total filling at the interface is similar but marginally increased, i.e., Ti\(^{0.62+}\), compared to Ti\(^{0.59+}\) in \(\delta\)-doped LTO.

In order to provide insight into the correlation strength within the two metallic layers, figure 8 finally shows the QP weight \(Z\) and the dimensionless electron–electron scattering \(\Gamma/k_B T\) for both doped titanates. The data is retrieved from the respective layer-dependent self-energies via 

\[
Z_{\omega} = \frac{1}{\Gamma(k_T Z)} \left( 1 - \frac{\partial}{\partial \omega} \Sigma(\omega) \right|_{\omega = 0} \right)^{-1}
\]

and

\[
\Gamma = -k_B T Z \text{ Im } \Sigma(0^+).
\]

Within the LTO interface layer the QP renormalization is weakly temperature dependent and with \(Z \sim 0.6\) still moderate. Also for the scattering rate the relation \(\Gamma/k_B T < 1\) holds up to high \(T\), marking regime III as coherent. Albeit true Fermi-liquid behavior, i.e., \(\Gamma/k_B T\) linear in \(T\), is only expected for very small temperatures well below the present range, the close-to-linear characteristics are notable. On the other hand the doped-Mott state in the next-distant layer has a stronger \(T\)-dependent QP weight, getting as low as \(Z \sim 0.2\) at \(T = 145\) K. Electron–electron scattering is here severe and strongly incoherent even at low \(T\). Similar observations hold for \(\delta\)-doped GTO, with overall somewhat increased correlation strength. Interestingly, the incoherent regime II seems on the way of restoring coherency at smaller temperatures, but \(\Gamma/k_B T\) for the similar \(|1\rangle\) character right at the interface deviates from quasi-linear behavior at very low \(T\).

Figure 5. Bond charge densities \(\rho = \rho_{\text{total}} - \rho_{\text{atomic}}\) for \(\delta\)-doped (a) LTO and (b) GTO. For each protocol, densities within (left) the \(ac\)-plane and (right) the \(bc\)-plane are given. The DFT+DMFT data is retrieved from calculations at \(T = 290\) K.
6. Electron states in δ-doped GdTiO₃ with broken spin symmetry

Finally we discuss possible ordering instabilities in the particle-hole channel. Both bulk materials LaTiO₃ and GdTiO₃ exhibit magnetic ordering at low temperatures, but because of the complexity of studying electronic ordering in the doped compounds we here restrict the investigation to only one system, namely, the GTO case. In the bulk, the compound becomes FM below 36 K, and the strongly enhanced spectral weight close to the Fermi level in the δ-doped case might be indicative of a Stoner-like magnetic instability. Furthermore, when doped with a SrO monolayer, roughly half of an electron is located at Ti ions right at the doping layer, which raises the question about in-plane Ti³⁺/Ti⁴⁺ charge ordering [48]. Concerning charge disproportionation or other possible intra-layer instabilities, we performed post-processing (or one-shot) DMFT based on the given projected multi-orbital onsite Hubbard Hamiltonian, now with intra-layer discrimination of both Ti ions, respectively. However, no checkerboard-type or other insulating instability was detected. Nonlocal Coulomb interactions may be relevant to trigger such orderings. A charge self-consistent treatment is not performed, since it asks for a symmetry lowering also in the DFT part, which renders the already heavy calculations very expensive. Therefore we still cannot fully exclude the possibility of an insulating solution. In the following we concentrate on broken spin-symmetry and shed light on a possible (in-plane) FM δ-doped state from a [100]-[010] interface architecture. Experimentally, ferromagnetism in SrTiO₃/GdTiO₃ quantum wells within a [110]-[001] interfacing has indeed been reported by Jackson and Stemmer [49].

In principle there are two magnetically active shells in GTO, namely, Gd(4f) and Ti(3d). Experimental work suggests that in the bulk an AFM coupling between Gd and Ti sets in at low T, giving rise to ferrimagnetism [50, 51]. But since the Gd-O-Gd and Gd-O-Ti exchange is believed to be weaker than the (FM) Ti-O-Ti one [50], we here approximate the problem by assuming the Gd sites paramagnetic without taking part in the formation of magnetic order. This is reasonable, since the temperature T = 145 K is also set way above the bulk $T_C = 36$ K.

![Figure 6. A]-integrated spectral function $A(ω)$ for δ-doped LTO from DFT+DMFT. (a) Total function compared to LDA (blue-grey), where $A(ω)$ builds on the 60 electron states from the bottom of the low-energy $t_{2g}$ manifold. Left: blow-up around $ε_F$. (b) Local Ti-resolved functions, with three electronic regions: orbital-ordered Mott insulating (grey background), orbital-polarized doped (light red background), and orbital-selective doped (light blue background). (c) Ti-resolved orbital fillings; black data points/line marks the respective total n.](image-url)
Post-processing (or one-shot) DMFT starting from the charge self-consistent paramagnetic DFT+DMFT solution does not lead to FM order. Using charge-only self-consistency, i.e., neglecting spin polarization in the KS-DFT part, also results in vanishing ordered moments. Only the complete spin-resolved charge self-

Figure 7. $\mathbf{k}$-integrated spectral function $A(\omega)$ for $\delta$-doped GTO from DFT+DMFT. The subfigures (a)–(c) are described as in figure 6.

Figure 8. Orbital-resolved quasiparticle weight $Z$ and dimensionless scattering rate $\Gamma/k_BT$ for the $\delta$-doped compounds. Full lines correspond to the states right at the SrO layer and the dashed line to the dominant doped Mott-state in the second-distant layer.
consistent treatment sustains magnetic order when starting from FM initialization at $T = 145$ K. Note that the latter protocol may overestimate magnetic-ordering tendencies, because once an exchange-splitting is introduced in KS-DFT via the DMFT Ti1–5 self-energies, it may not be easily suppressed within the formalism. On the other hand, taking into account spin polarization in the KS part may be vital. Moments on the ligands and corresponding exchange is important for the overall lattice magnetic ordering.

A total moment of 6.8 $\mu_B$ is obtained for the whole 100-atom supercell with the 20 Ti ions. The material remains in a net metallic regime, as visualized in figure 9(a) when plotting the total spectral function. Both QP as well as the incoherent lower Hubbard peak are spin polarized, suggesting a mixed behavior of localized and itinerant ferromagnetism. Though initialized as coherent FM, inspecting the real-space ordering interestingly reveals that the system displays at convergence a ferrimagnetic ordering (see figures 9(b) and (c)). The FM metallic layers with Ti1–2 and the FM Mott-insulating layers with Ti3–5 couple antiferromagnetically, whereby the PM characterization via regimes I–III remains intact in the spin-polarized case. Within the FM orbital-ordered Mott regime the Ti3–4 ions also show nearly complete spin polarization. But the most distant Ti5 ion surprisingly carries a smaller magnetic moment. Exchange coupling to the metallic FM layers thus seems to increase the ordered moment. These layers in regime II/III are more weakly spin polarized, with a dominant $d_{xy}$ weight nearest to the SrO doping layer.

The ferromagnetism in the Mott regime is reminiscent of the corresponding ordering of bulk GTO [12]. In the case of the itinerant TiO$_2$ layers, a combined intra- and inter-layer double-exchange-like mechanism [52, 53] may contribute to FM tendencies in the interface region with different structural distortions. A diverse exchange mechanism therein may also be evident from the AFM coupling of Ti to the apical oxygens (see figure 9(b)), whereas in the Mott layers these ligands appear ferromagnetically coupled to the titanium ions. The reason for the AFM coupling of both parts appears more subtle. On the basis of the Goodenough–Kanamori rules [54, 55], it could be related to the ‘more 180°-like’ orientation of the nearby Ti2–3 [1] orbitals, evident from

![Figure 9](image-url)
the weaker rotation in the \(bc\)-plane on Ti2 compared to Ti4 in figure 9(b). The total-energy competition between the paramagnetic and ferrimagnetic state is rather tight, favoring the magnetic order by about 10 meV/atom.

7. Summary and discussion

Starting from the Mott-insulating bulk compounds \(\text{LaTiO}_3\), and \(\text{GdTiO}_3\), we investigated the rich and complex electronic structure originating from \(\delta\)-doping with an SrO monolayer in a superlattice architecture along the [001] direction. The realistic multi-orbital setup with 10 TiO\(_2\) layers in between the doping layers allows us to differentiate various correlation regimes with distance to SrO by the elaborate DFT+DMFT method. An orbital-selective itinerant state at the interface changes into an itinerant orbital-polarized doped-Mott state, which transforms to an orbital-ordered Mott-insulating region at a larger distance. Notably, that Mott regime displays even stronger orbital polarization than the bulk-insulating case. The transport within the itinerant layers is of a mixed Fermi-liquid-like- and incoherent character. Generally, the \(\delta\)-doped GTO case promotes somewhat stronger correlation effects than \(\delta\)-doped LTO above the respective ordering temperatures.

Our study reveals the intricate interplay between structural distortions and the electrons’ charge, orbital, and spin degrees of freedom in the heterostructure. The layer- and temperature-dependent transitions between the encountered electronic phases pose novel challenging problems in strongly correlated electron systems. For instance, further theoretical investigations are necessary to shed light on the dependence on the number of SrO layers. Concerning comparison with experiment, our concrete work serves as a theoretical prediction, since to our knowledge the here studied canonical [100], [010] interface geometry for \(\delta\)-doped titanates has so far not been experimentally investigated. There are recent experimental works on [110], [001] interfaces \([8,42,43]\) that find an overall insulating state for \(\delta\)-GTO. This different finding may indeed be traced back to the differences in the interface geometries. Whereas the ([100], [010]) interface is nearly perfectly flat in our calculation, the ([110], [001]) one shows some buckling \([42]\), which we can confirm \([56]\). Note that due to the different orientations, the square-like interface Ti sublattice has much stronger rectangular distortion in the ([110], [001]) geometry. This could more easily trigger the Ti\(^{3+}/\text{Ti}^{4+}\)-like charge ordering as one option to form the insulating interface state. Furthermore, the distinct orbital-ordering in Mott-insulating titanates is not easily commensurate across the ([110], [001]) geometry, which might lead to a symmetry-breaking of the original GTO orbital ordering based on the [1] state aligned predominantly along the \(a\)-axis.

Allowing for spin ordering results in a further enrichment of the already sophisticated electronic structure. A ferrimagnetic ordering, again with itinerant and Mott-insulating regimes, settles in \(\delta\)-doped GTO. It results from the subtle exchange-interaction variations due to the differences in structural distortions and orbital occupations, as well as degree of itinerancy.

The present work renders it obvious that the electronic structure characteristics in oxide heterostructures are in principle likely to cover the full plethora of many-body condensed matter physics within a single (designed) compound. From another perspective, this generates vast room for engineering and creating novel states of matter.

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