The doping induced insulator-metal transition in \( La_{1-x}Sr_xTiO_3 \) is studied using the ab-initio LDA+DMFT method. Combining the LDA bandstructure for the actual, distorted structure found recently with multi-orbital DMFT to treat electronic correlations, we find: (i) ferro-orbital order in the Mott insulating state without orbital degeneracy, (ii) a continuous filling induced transition to the paramagnetic metal (PM) with \( x \), and (iii) excellent quantitative agreement with published photoemission data for the case of 6\% doping. Our results imply that this system can be described as a Mott-Hubbard system without orbital (liquid) degeneracy.

PACS numbers: 71.27.+a, 71.15.Mb, 79.60.-i

The early TMO \( LaTiO_3 \) is an interesting case of a system exhibiting filling-driven insulator-metal transition. Long thought of as a text-book example of a Mott insulator with antiferromagnetic order, current interest in orbital correlations in TMOs has reopened the subject of the physics of \( LaTiO_3 \) [1].

According to [2] this material with \( Ti^{3+}(3d^1) \) configuration is an electron analog of the cuprates, with \( G \)-type AF spin order below \( T_N \approx 150 \) K, and with a reduced spin moment in the AF state. Recent neutron scattering measurements reveal an *isotropic* magnon dispersion, with a small spin gap, \( \Delta_s = 3.3 \) meV, putting strong constraints on an acceptable mechanism for the observed antiferromagnetism [2]. The fact that the single electron in \( LaTiO_3 \) resides in the \( t_{2g} \) orbitals (less prone to Jahn-Teller distortions) suggested that the orbital moment might not be fully quenched in this case. Attempts to explain the strongly reduced spin moment of \( \mu = 0.46 \mu_B \) [2] assuming an unquenched orbital moment aligned antiparallel to the spin moment (spin-orbit coupling in the \( t_{2g} \) shell of \( Ti^{3+} \) led to a spin gap much larger than that of 3.3 meV observed in INS [2], excluding an orbital contribution to the ordered moment. Moreover, ferro-orbital order (FOO) has recently been suggested [3], in complete accord with the \( G \)-type AF spin order below \( T_N \), implying lifting of the \( t_{2g} \) orbital degeneracy.

The metallic phase in \( La_{1-x}Sr_xTiO_3 \) [1] has been shown to be a canonical strongly correlated Fermi liquid [1], putting additional constraints on an acceptable model for this system. In particular, this implies a non-degenerate ground state in the paramagnetic metal (PM) phase, since any remnant of orbital degeneracy (if it was hypothesized to exist) would lead to violation of Landau’s Fermi liquid hypothesis, and lead to a non-FL metallic state, in contradiction with observations. AF LRO is rapidly suppressed upon \( Sr \) doping, and classic signatures of the Brinkman-Rice (BR) correlated FL are seen close to the MIT, suggesting that the AFI state is a Mott-Hubbard insulator and that the AFI-PM transition is a Mott-Hubbard transition. Given the incomplete understanding of the AFI, the mechanism of the MIT still constitutes an open problem for theory, in spite of much recent activity [4].

Two alternatives were proposed to account for the puzzling observations in the AFI phase. Mochizuki et al. [5] presented a model for the AF in \( LaTiO_3 \) using a \( GdFeO_3 \) distortion, which, however, was not observed. Khalilullin et al [6] proposed a novel theoretical idea based on an orbital liquid, but the short-ranged orbital RVB-like fluctuations were not observed either [3]. Moreover, it has been shown recently that long range AF order is theoretically incompatible with an orbital liquid state [7], deepening the controversy regarding the origin of \( G \)-type AF order in \( LaTiO_3 \).

Here, following new work [8] pinpointing the real crystal structure (RCS) of \( LaTiO_3 \), we propose a detailed theoretical scenario unifying the various experimentally observed features in the insulating (I) as well as the correlated metallic (M) states. Employing the state-of-the-art technique LDA+DMFT (IPT) (combining the real bandstructure of \( LaTiO_3 \) with dynamical correlation effects of local Coulomb interactions), we show how a consistent description of the doping-induced insulator-metal (I-M) transition, as well as very good quantitative agreement with photoemission results is obtained.

The RCS of \( LaTiO_3 \) (i.e, \( Pbam \) space group) involves a structural distortion arising from the tilting of the \( TiO_6 \) octahedra around the \([110]\) axis followed by their rotation around \( c \), beginning from the cubic perovskite structure. The specific distortion of the \( TiO_6 \) octahedra in \( LaTiO_3 \) is characterized by a large splitting in the \( O2-O2 \) edge lengths of the octahedral basal plane, giving rise to elongation along \( a \) and shrinking along \( b \). This implies FOO and a lifting of \( t_{2g} \) orbital degeneracy. Starting from a local picture in the \( d^1 \) configuration, the occupied orbital is constructed as: \( |a| = 0.77(\frac{x^2+y^2}{\sqrt{2}}) \pm 0.636|xy| \), which is non-degenerate [8]. We have carried out a local density approximation (LDA) study based on the RCS described above.
The character of the occupied ground state orbital (not shown) is in accord with the result of Ref. [8]. The LDA transfer energy (LDA) is large, $\Delta$ shown, is in accord with the result of Ref. [8]. The LDA on-site Hubbard $U$ configuration, with the two $d$ electrons on different orbitals, realized upon $d-d$ hopping, and the inter-orbital coupling, $U' = (U - 2J_H) \simeq 4.0$ $eV$. These results (see Fig. 1) do not represent an insulating state, this requiring a proper treatment of correlation effects in the RCS. Given the FOO found in LaTiO$_3$, a description in terms of a single-band model for the $\alpha$ band is untenable, and requires a full multi-orbital dynamical mean field calculation. To avoid double counting of interactions already treated on the average by LDA, we follow [4] to write,

$$H'_0 = H_0 + \sum_{\alpha\sigma} \epsilon^0_{\alpha\sigma} n_{\alpha\sigma},$$

with $\epsilon^0_{\alpha\sigma} = \epsilon_{\alpha\sigma} - U (n_{\alpha\sigma} - 1) + \frac{U}{4} (n_{\alpha\sigma} - 1)$. The full many-body Hamiltonian is now given by,

$$H = H_0' + U \sum_{\alpha\sigma} n_{\alpha\sigma} + U' \sum_{\alpha\beta} n_{\alpha\sigma} n_{\beta\bar{\sigma}} - J_H \sum_{\alpha\sigma} \textbf{S}_{\alpha\sigma} \cdot \textbf{S}_{\alpha\bar{\sigma}}.$$
be 0.15 eV, implying a reduction in the charge transfer energy, $\Delta_{ct} = (\epsilon_p - \epsilon_d)$ from 7.0 eV in the LDA to 6.64 eV in the correlated solution. This is likely to be an overestimate, since further downward renormalization of $\Delta_{ct}$ will result from additional Hartree shifts arising from inclusion of Madelung ($p-d$ interaction) terms. These results constitute a concrete resolution of the questions posed recently [15], namely, the mechanism for the generation of a small-gap Mott-Hubbard insulator in a situation where the Coulomb interactions are comparable to the LDA bandwidth. In view of our results, dynamical effects of coupled spin/orbital correlations in the real structure of $\text{LaTi}_3\text{O}_5$ are of crucial importance for a consistent resolution of this issue. We also find the occupation of the lowest $t_{2g}$ orbital, $n_\alpha = 0.17$, slightly higher than that of the other two higher-lying (by 0.15 eV) orbitals in the $t_{2g}$ sector.

These results are consistent with having ferro-orbital order (FOO) in $\text{LaTi}_3\text{O}_5$ [3]. Further, since the ground state occupied orbital, $|\alpha\rangle = a_1|xz + yz\rangle + a_2|xy\rangle$ (consistent with Ref. [8]) is not oriented along one of the bonds, the resulting AF exchange is not expected to be very anisotropic. A detailed calculation of the Heisenberg superexchange based on the LDA+DMFT results, along with proper incorporation of spin anisotropies, is in progress and will be reported elsewhere.

To model the paramagnetic metallic (PM) state, reached (continuously from the PI in our approach) upon doping $\text{LaTi}_3\text{O}_5$ with $\text{Sr}$, we extended our calculation for the PI to: (i) incorporate the change in band-filling along the same lines as for generalized IPT for the single band case. This implies computing the chemical potential shift, as required by Luttinger’s theorem, and, (ii) considering the effects of $\text{Sr}$ doping induced static disorder (the difference of the on-site potentials on $\text{Sr}$ substitution is $\Delta v \simeq 4.0 \text{ eV}$ [16]) using the coherent-potential approximation (CPA) combined self-consistently [17] with the multi-orbital IPT described above. Furthermore, to obtain quantitative consistency with spectroscopic results, we found it necessary to include the (small near $E_F$) DOS of the $e_g$ bands found in the LDA (Fig. 1), as well (see below).

Generically, hole doping the (Mott) PI creates a very sharp, quasicoherent Fermi liquid peak at the renormalized $E_F$, with dynamical spectral weight transfer over a large energy scale from high to low energy (caused by $U, U', J_H$ within DMFT), driving a first-order Mott transition in the generic case. In this situation, static, potential disorder is expected to lead to a moderate broadening of the sharp FL peak, with spectral weight transfer from low to high energy [17], and, more importantly, to convert the first-order Mott transition into a continuous one. Thus, the character of the MIT, as well as details of the actual one-particle spectrum depend sensitively on how the competition between Mott-Hubbard localization and itinerance in a multi-band system is affected by doping induced static disorder.

With this in mind, we show the photoemission (PES) and inverse-PES (IPES) spectra for the lightly (\( \delta \equiv x+y = 0.06 \) doped, PM state of $L_a\alpha_2\text{Sr}_1-x\text{Ti}_3\text{O}_5+y/2$ [18]), along with the experimental result for $I_{\text{PES}}(\omega)$ in Fig. 3. Clearly, excellent quantitative agreement between theory and experiment is found over the entire range $-2 \leq \omega \leq E_F$. In particular, the lower Hubbard band, the quasicoherent FL feature, as well as the details of the lineshape are all in excellent agreement with experiment. In the IPES spectrum, we are able to resolve the $\alpha, \beta$ peaks

![FIG. 2. LDA+DMFT results for the partial DOS in the insulating state, obtained using $U = 6.0$ eV, $J_H = 1.0$ eV, and $U' = 4.0$ eV in the real bandstructure of $\text{LaTi}_3\text{O}_5$.](image1)

![FIG. 3. The photoemission (PES) and inverse photoemission (IPES: in inset) spectra for both, pure (dashed) and doped (solid) $\text{LaTi}_3\text{O}_5$. Excellent quantitative agreement with experimental results (PES: squares) of Ref. [18] is clear.](image2)
along with the much greater signal intensity and the correct detailed form of the lineshape [19]. Thus, our results represent a quantitatively accurate representation of the complete one-electron spectral function in the PM phase of $La_{1-x}Sr_xTiO_3+y/2$. Lastly, from the Fermi liquid self-energies (not shown), the effective mass renormalization is estimated to be $m^*/m^0 = 1.5$ for $\delta = 0.06$ in good quantitative agreement with the frequency-dependent renormalization estimated from PES [18]. Actually, the total renormalization includes additional renormalization (factor of 2) coming from the $k$-dependence of the self-energies. On general grounds, we do expect such renormalization in a case of proximity to the AF transition; theoretically, an extension to include non-local correlations is required to address this issue. We have not done this here.

We stress essential differences between our work and earlier works. In Ref. [4,5], an incorrect crystal structure was used for the LDA calculation. Moreover, the strong earlier works. In Ref. [4,5], an incorrect crystal structure was used for the LDA calculation. Moreover, the strong

The DMFT equations forces a restriction to high-$T$ requires the solution of the DMFT equations at $T \approx 150 \text{ K}$ [21]. Given the strong $T$ dependence of the correlated Fermi liquid scale within DMFT, as well as the much lower FL coherence scale observed experimentally in doped $LaTiO_3$ [1,13], (in contrast to QMC results), we believe that a quantitative comparison with experiment at low $T$ requires the solution of the DMFT equations at lower $T \approx 150 \text{ K}$, as we have done. Finally, we draw attention to the excellent quantitative agreement between theory and experiment for the one-electron spectral function, obtained using LDA+ (multi-orbital) DMFT. To our knowledge, this is the first calculation achieving such unprecedented agreement between experiment and theory for this system.

To conclude, we have studied the doping induced Mott transition in the $3d^1$ system $La_{1-x}Sr_xTiO_3$ using the $ab$-initio LDA+DMFT method. Starting from the real crystal structure (with lifting of $t_{2g}$ orbital degeneracy), we have explicitly demonstrated the nature of the carrier driven MIT in this system. Our results support ferroorbital order in the insulating state, consistent with recent suggestions [3], and with the observed $G$-type AF order. In conjunction with [8, 21], these results favor a description of the physics of $LaTiO_3$ in a picture of non-degenerate $t_{2g}$ orbitals. Within this picture, in the PM state, excellent quantitative agreement with published PES and IPES results is obtained, providing a complete description of the evolution of one-particle excitations across the MIT. Similar ideas can be fruitfully applied to study the doping-driven MI transitions in other TMO-based systems [20] with coupled spin-orbital correlations.

ACKNOWLEDGMENTS

MSL and LC acknowledge fruitful discussions with D. I. Khomskii in course of this work. SL wishes to acknowledge A. Yaresko for his help with the LMTO program and for valuable discussions. Work carried out under the auspices of the Sonderforschungsbereich 608 of the DFG (Köln), and the MPI-CPfS (Dresden).