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Mott-Hubbard and filling-controlled electronic transitions in the layered cuprate oxides

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We investigate the one-particle spectral properties of La_2CuO_4. Contrary to conventional wisdom, our dynamical mean-field theory results elucidate the Mott-Hubbard nature of the insulating state in this and related d^9 planar compounds. This is shown to be driven by the interplay between covalency and strong local electronic correlations. Good qualitative agreement with photoemission and soft-x-ray absorption is found in the paramagnetic insulating phase. Upon doping, we obtain inhomogeneous charge (electron, hole) responses which are relevant for understanding the evolution of the correlated electronic structure near the filling-controlled insulator-to-metal transition in late transition-metal oxides.

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Over the last decade, many experimental[1–10] and theoretical efforts[11–18] have been dedicated to resolve the correlated nature of many-body excitations and how chemical doping influences the one-particle spectra of layered cuprate oxides. However, due to the nontrivial competition between strong on-site Coulomb interactions on the copper sites and their coupling (covalency) with neighboring oxygens, the electronic structure of the CuO_2 planes turns out to be difficult to be described theoretically.[14–16] In this work we present a comprehensive many-body description for the electronic excitations of La_2CuO_4 in view of understanding its paramagnetic (PM) insulating phase. Based on a three-band Hubbard model similar to the one introduced by Emery and Varma *et al.*,[12] we concentrate on the relevant aspects of the in-plane orbitals, with attention to the dynamics of the Hubbard bands, including the Zhang-Rice (ZR) singlet (ZRS),[13] and the changes in the electronic structure across the doping-driven metal-insulator transition (MIT).

Historically, the three-band Hubbard (Emery) model[12] takes into account both oxygen p and the copper $d_{x^2-y^2}$ orbital. Based on this model, ZR (Ref. 13) demonstrated that the low-energy physics of the hole-doped superconductors can be mapped onto a single-band model. In their picture, an extra hole added into the oxygen band binds strongly with a hole on the copper site, forming a Cu-centered singlet: the ZRS. Motivated by the ZR phenomenology, Collart *et al.*[10] recently pointed out that the correlated nature of the MIT in cuprates is closely related to both the ZR *band* (ZRB), which lies at the top of the valence band,[7] and of the upper Hubbard band (UHB).[2] In this work we *formulate* precisely this problem. We describe the formation of p,d lower Hubbard bands (LHBs) and UHBs in the PM insulating phase of La_2CuO_4, showing how they evolve upon electron and hole doping. The resulting correlated electronic structure is in qualitative agreement with photoemission spectroscopy (PES) and soft-x-ray absorption spectroscopy (SXAS) data. Further, the moderately hole-doped regime shows an *anomalous* spectral weight transfer (SWT) characterized by the *absence* of new electronic states near the Fermi level (E_F) in agreement with experiment.[6,19]

Experimentally, the physical properties of Cu-O systems have been studied intensively in view of understanding the evolution of their electronic structure with doping near the filling-controlled MIT (Refs. 2, 3, and 5–7) and the dynamical nature of the ZRB.[9] These experimental observations have provided us with valuable information on the Cu 3*d* states, including the *dd* excitations and the ZRB formation. We recall here the work by Taguchi *et al.*[9] where the valence-band excitations of two families of cuprate compounds were probed in detail, showing that the ZRB feature is present in La_2CuO_4 even at room temperature. Motivated by this result, we explore the effect of *dd* electron-electron interactions in a *pd* model for cuprates. By treating the effect of local strong Coulomb interactions in the 3*d* shell within the dynamical mean-field theory (DMFT) we show how an effective three-band (Emery) model captures the essential aspects of the valence and the conduction bands in the normal state of La_2CuO_4. Our work provides a consistent picture for the PM insulating phase of d^9 layered cuprates and its dynamical suppression upon doping.

Theoretically, Refs. 14–18 are a few examples among the various investigations[11] which highlight important aspects concerning the doping dependence of different Cu-O bands, the evolution of the correlated one-particle spectra near E_F, and the low-energy magnetic properties of the CuO_2 planes. However, no theoretical study has been yet performed to explain the Mott-Hubbard nature of undoped La_2CuO_4 vis-à-vis with experimental findings; we do this in this work. Based on our agreement with experiment, we argue that the dynamical SWT (between bands with different orbital symmetries) restricts the validity of mapping Emery type of models onto extended one-band Hubbard models.[11,16] In our description for the low- and high-energy excitations in La_2CuO_4 we assume that the layer-related one-particle features can be described by a tight-binding model which consists of three orbitals, i.e., Cu $3d_{x^2-y^2}$ and the O $2p_x, 2p_y$ bands.[14–17] The corresponding Hamiltonian, which also includes the Coulomb interaction (U) term between two electrons in the same copper site, reads

$$\begin{aligned} H = {} & \sum_{i\sigma} (\varepsilon_d - \mu) d_{i\sigma}^{\dagger} d_{i\sigma} + (\varepsilon_p - \mu)[p_{i\sigma}^{\dagger} p_{i\sigma} + \bar{p}_{i\sigma}^{\dagger} \bar{p}_{i\sigma}] \\ & + \sum_{\mathbf{k}\sigma} \{\varepsilon_{p\mathbf{k}}[p_{\mathbf{k}\sigma}^{\dagger} p_{\mathbf{k}\sigma} - \bar{p}_{\mathbf{k}\sigma}^{\dagger} \bar{p}_{\mathbf{k}\sigma}] + \alpha_{\mathbf{k}}[p_{\mathbf{k}\sigma}^{\dagger} \bar{p}_{\mathbf{k}\sigma} + \bar{p}_{\mathbf{k}\sigma}^{\dagger} p_{\mathbf{k}\sigma}] \\ & - 2t_{pd} \gamma_{\mathbf{k}}[d_{\mathbf{k}\sigma}^{\dagger} p_{\mathbf{k}\sigma} + p_{\mathbf{k}\sigma}^{\dagger} d_{\mathbf{k}\sigma}]\} + U \sum_i n_{i\uparrow}^d n_{i\downarrow}^d . \qquad (1) \end{aligned}$$

Here, ε_d (ε_p) is the atomic energy of copper (oxygen) sites, μ is the chemical potential, and t_{pd} is the Cu-O (hybridization) hopping integral. $\varepsilon_{p\mathbf{k}}=-\frac{8t_{pp}}{\gamma_{\mathbf{k}}^2}\sin^2 k_x \sin^2 k_y$ is the O_{2p} band dispersion and $\gamma_{\mathbf{k}}^2=\sin^2 k_x+\sin^2 k_y, \alpha(\mathbf{k}) =\frac{4t_{pp}}{\gamma_{\mathbf{k}}^2}\sin k_x \sin k_y(\sin^2 k_x-\sin^2 k_y)$ are form factors corresponding to the two-dimensional square lattice of copper oxides. In Eq. (1), $p_{\mathbf{k}\sigma}$ ($\bar{p}_{\mathbf{k}\sigma}$) represents the hybridizing (nonhybridizing) Wannier O_{2p} orbitals in momentum space representation and the d operators describe the $3d_{x^2-y^2}$ correlated orbital. The bare (one-particle) Hamiltonian corresponding to Eq. (1) in matrix form is[15]

$$\hat{H}_0(\mathbf{k})=\begin{bmatrix} \varepsilon_d & -2t_{pd}\gamma_{\mathbf{k}} & 0 \\ -2t_{pd}\gamma_{\mathbf{k}} & \varepsilon_p+\varepsilon_{p\mathbf{k}} & \alpha_{\mathbf{k}} \\ 0 & \alpha_{\mathbf{k}} & \varepsilon_p-\varepsilon_{p\mathbf{k}} \end{bmatrix}. \tag{2}$$

In this compact form the corresponding one-particle Green's function (GF) reads $\hat{G}_0^{-1}(z,\mathbf{k})=z+\mu-\hat{H}_0(\mathbf{k})$. Within this notation the full lattice Green's functions are defined by the inverse of the Dyson equation,

$$[z+\mu-\hat{H}_0(\mathbf{k})-\hat{\Sigma}(z)]\hat{G}(z,\mathbf{k})=\hat{\mathbf{1}}. \tag{3}$$

We treat the dynamical effects of strong on-site dd-Coulomb interactions in $D=\infty$ using iterated perturbation theory (IPT) as an impurity solver. The DMFT solution involves replacing the lattice model by a self-consistently embedded asymmetric Anderson impurity model and a self-consistency condition requiring the local impurity GF to be equal to the local GF for the lattice. The self-energy $\hat{\Sigma}(z) \equiv\Sigma_d(z)$ on the Cu site is computed within the IPT scheme. The equations for the IPT are the same as those of Refs. 20 and 21; we refer the reader to these references for details.

To proceed we will employ typical parameters for the three-band Hamiltonian to model the CuO_2 planes of La_2CuO_4 as in previous publications,[14,16,17] i.e., $t_{pd}=1.3$ eV, $t_{pp}=0.65$ eV, $\Delta=3.6$ eV,[22] and $\varepsilon_p=\varepsilon_d+\Delta$. To keep the number of adjustable parameters small we chose $\varepsilon_d=-U/2$; therefore the only free parameter in our theory is the strength of Coulomb interaction U. To obtain the orbital occupations the DMFT equations are constrained by the sum rule, $\langle n_{\text{tot}}\rangle =\int_{-\infty}^{\mu}\rho_{\text{tot}}(\omega)d\omega\equiv n_t$. The chemical potential μ is then determined self-consistently within the DMFT loop at each stage using $\rho_{\text{tot}}(\omega)$ computed in each iteration. In addition, the chemical potential of the *effective* bath μ_0 is calculated with the condition that $\langle n_d\rangle=\langle n_d^0\rangle$ (Ref. 23) and the process is iterated to convergence. The last condition is used to account for the correct low-energy behavior of the self-energy in a way consistent with Friedel-Langreth sum rule.[21]

Our results for $n_t=5$ (one hole per plaquette) are shown in Fig. 1. As seen in this figure, the Hubbard U introduces large SWT driving the system into a Mott-Hubbard insulating state. According to our scheme the MIT takes place for $U(\equiv U_c)$ between 9.5 eV $<U<$ 10 eV. For $U\geq 10$ eV the system is insulating with a clear Mott-Hubbard gap at lower energies. LHBs and UHBs are visible in the d and p sectors. Due to the fact that the $d_{x^2-y^2}$ orbital is strongly hybridized with the p bands, the Mott-Hubbard insulating state is also manifested in these bands. This high order effect suggests that the most relevant many-body scattering processes emerging in *covalent* material are governed by those taking place on correlated sectors.[24] Within our treatment E_F resides in the vicinity of the bottom of the conduction band, differently from experimental works suggesting that it is placed on the top of the valence band[7] or in the middle of the charge gap.[8] The upper panels of Fig. 1 show that an appreciable amount of spectral weight is transferred from low to high energies with increasing U. There is an overall enhancement of the UHB, which splits off from the low-energy conduction states of the correlated d band. Consistent with Ref. 3 the character of the UHB is predominantly Cu $3d$-like with an admixture of about 6% (12% in Ref. 3) of O_{2p} states. The lower part of the spectra deserves more attention due to the formation of the ZRB. We interpret the bands between 2 and 4 eV binding energies as being the ZRBs since they have strong mixed pd character and are originated from mutual scattering processes within the d states. The width of the ZRB estimated from our calculation for $U=10$ eV is ≈ 2 eV and the spectral weight (ψ) per spin of the ZRBs is $\psi_{d,p} =(0.274,0.137)$, indicating that in the large U limit the ZRB has preferentially a bonding d band character at half-filling.

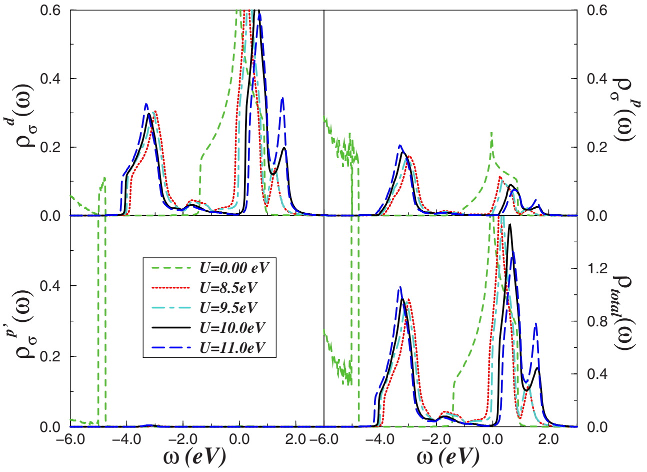

FIG. 1. (Color online) Orbital resolved and total DOS for different values of U and $n_t=5$. Here, $p'\equiv\bar{p}$. Notice the transfer of spectral weight from low to high energies across the MIT.

Figure 2 shows the theory-experiment comparison for the total intensity in the PM insulating phase of La_2CuO_4. Our results for $U=10$ eV are compared with room-temperature PES (Ref. 9) data as well as with SXAS.[2] As seen, good qualitative agreement over almost the whole energy scale from -3.5 eV $\lesssim\omega\lesssim 1.5$ eV is observed. Several features of the PES and inverse photoemission (IPES) spectra can be interpreted in the light of our result. First, our spectra contain low lying excitations at energies up to 1.5 eV binding energy in agreement with experimental data. Below -2 eV the ZRB starts growing, also in agreement with experiment. Further, broad spectral features made up from incoherent-scattering processes are also well captured within our theory. Of importance here is the width of the UHB which is in (qualitative) good agreement with SXAS spectra. Thus, our $U=10$ eV solution represents a good qualitative description of basic PES and IPES data for the PM insulating phase of

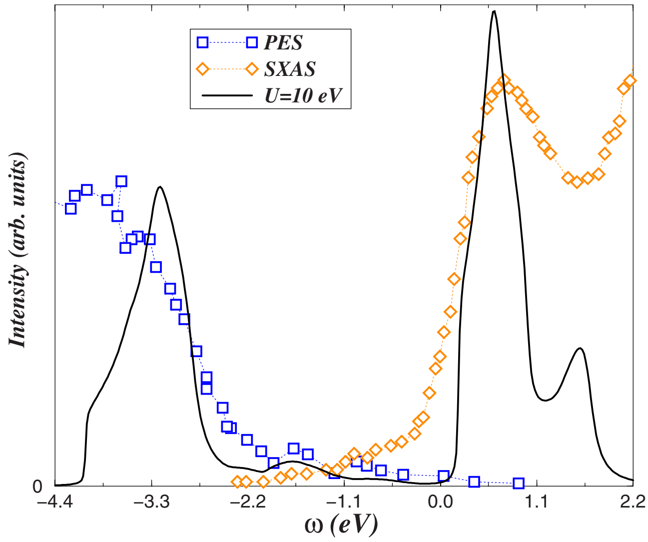

FIG. 2. (Color online) Comparison between our results for total DOS ($U=10$ eV) with x-ray PES and soft-x-ray absorption (SXAS) of La_2CuO_4. Experimental data for SXAS and PES are taken, respectively, from Refs. 2 and 9. The intensity of the experimental curves is normalized to coincide with theory. Notice that above 1.5 eV and below −4 eV other bands [not included in Eq. (2)] start to play a role (Refs. 3 and 25); thus our theory is understood to work only up to these energies.

La_2CuO_4. However, it deserves to remark that our results for PES below −4 eV differ from the experimental ones because of the lack of additional (valence) bands[3,25] in the one-particle Hamiltonian, $\hat{H}_0(\mathbf{k})$. In addition, we recall that in experimental data surface and background like contributions are often subtracted making the spectra very smooth. This may have had the effect of decreasing the weight in some regions making a full comparison between theory and experiment difficult.

Our DMFT results for the insulating state of La_2CuO_4 (Fig. 1) imply that the charge gap of layered cuprates is caused by strong on-site Coulomb repulsion U. In Fig. 2 we show that the most salient features of the one-particle spectral function are well described with few parameters, namely, U ($\equiv U_{dd}$), the charge-transfer (CT) energy Δ, the O_{2p} band dispersion, and the pd hybridization [see Eq. (1)]. We shall notice, however, that Zaanen, Sawatzky, and Allen (ZSA) (Ref. 26) proposed a classification scheme for transition-metal compounds, where late transition metals are so-called CT insulators. NiO and CuO are classical CT-type compounds, where $U > \Delta$. In their theory, electrons and holes behave differently in CT insulators: electrons are more correlated (heavy d particles) than holes (light anions forming the valence band). This situation is different for early transition metals, where $\Delta > U$.[26] Indeed, early transition metals are canonical Mott-Hubbard insulators in the sense that *both* holes and electrons move in correlated d bands. It is important at this point to notice that our theory is consistent with the ZSA classification scheme since the critical U_c needed to obtain the Mott-Hubbard gap is larger than the charge-transfer energy Δ, $U_c > \Delta$. Given the strong covalency and the large U_c compared to Δ, we find for the Mott-Hubbard *insulating* (half-filled) phase that the correlated states near E_F have more Cu 3d character than O_{2p} character. According to our calculation most of the O_{2p} spectra are found below the ZRB, in agreement with experimental PES spectra.[9] Our picture thus differs from the accepted wisdom for CT insulators, where the O_{2p} band sets in between the LHB and the UHB and the insulating gap is formed between the O_{2p} and the UHB. Such a multiband framework for the correlated electronic structure of CT insulators seems to be valid within the configuration-interaction approach, which assumes that the electronic properties are local. (The valence-band spectrum within this approach is obtained from a single-site cluster model with full multiplets in the local symmetry.[27]) However, in our theory the insulating gap is driven by dynamical SWT from low to high energies (LHB and UHB), whose local U is screened by the ligand pd (strongly momentum dependent) hopping. As already discussed, the O_{2p} spectral density of states (DOS) near E_F follows the 3d evolution—this together with the dynamical screening of the Coulomb interaction are key signatures of strongly hybridized systems. Thus, due to the nontrivial interplay between covalency and large U, the insulating gap of La_2CuO_4 should be understood as a Mott-Hubbard insulator. On the theoretical side, our DMFT results for $n_t=5$ call into question the schematic illustration[28] of the energy levels used to assign the band character of undoped La_2CuO_4 and related d^9 compounds.[9,29]

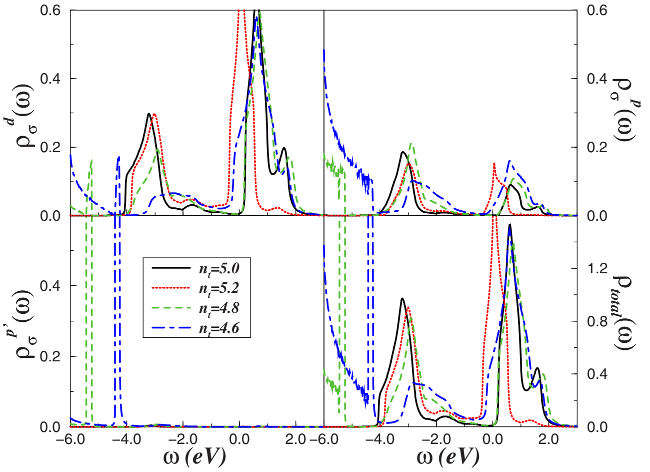

FIG. 3. (Color online) Orbital resolved and total DOS for $U=10$ eV and different total occupations. As in Fig. 1, $p' \equiv \bar{p}$. Notice the transfer of spectral weight upon doping and the insulating behavior at $\langle n_t \rangle = 4.8$.

We now turn to the evolution of the correlated electronic DOS of Eq. (1) away from half-filling, $n_t \neq 5$. This problem is concerned with the nature of the charge carriers in doped cuprates and the evolution of its electronic structure across the filling-controlled MIT.[1,2,5–7] The DOSs corresponding to electron ($n_t=5.2$) and hole ($n_t=4.8, 4.6$) doping cases are shown in Fig. 3. It is found that chemical doping transfers spectral weight over large energy scales between the UHBs and the LHBs. Upon electron doping the ZRB formed in the d sector becomes more populated, showing that electrons have mostly d character in La_2CuO_4. On the other hand, its weight is considerably reduced when holes are introduced in the system. The spectral weight of the ZR d band is simultaneously transferred to the energies above E_F and to the p-ZRB, demonstrating the p character of the carriers upon hole doping. The overall spectra are pushed toward E_F, indicating that the effective chemical potential is renormalized by chemical doping. However, whether or not the dynamical SWT between the ZR (LHBs) bands and the Kondo-type states near E_F plays an important role in superconductivity[30] remains to be investigated.

According to our treatment the insulating gap closes discontinuously; thus the MIT upon electron or hole doping (without incorporation of intrinsic chemical disorder)[31] is found to be first order. However, the localized phase appears to be stable toward small hole concentrations, see our result for n_t=4.8, indicating that holes are tightly bound to copper ions. The absence of a metallic state in the light-to-moderately doped regime is consistent with various experimental studies,[6,19] showing an insulating state before the pseudogap-type line shape starts to develop around E_F. Our result for n_t=4.8 suggests that the unusual insulating state in the underdoped region of $La_{2-x}Sr_xCuO_4(x<0.15)$ (Refs. 6 and 19) is determined by the interplay between the 2D network and the correlation induced Mott-Hubbard insulating state.

The hole-doping induced first-order transition reflects the correlated nature of the insulating state, which is built up from asymmetric incoherent-scattering processes in the $d_{x^2-y^2}$ orbital. While high energy states are modified upon hole doping, those at low energies (near E_F) remain practically as that of the parent insulator at small carrier concentrations. It is interesting to note that large SWT from the d-ZRB to the p one is taking place at n_t=4.8 compared to n_t=5. The correlated DOS near E_F (Fig. 3) appears to be insensitive to the changes taking place at higher energies. This behavior is in good agreement with large changes found in the optical conductivity spectra of Sr-doped La_2CuO_4 (Ref. 1) at energies above 2 eV. Our results, thus, provide a consistent picture for the large changes observed in the one- and two-particle spectral functions across the doping induced insulator-(bad) metal transition in La_2CuO_4.

In conclusion, we have shown how the three-band (Emery) model treated with the DMFT (IPT) approximation yields a reliable qualitative description for the one-electron spectral function in the paramagnetic insulating phase of La_2CuO_4. In the undoped regime we found that the metal-insulator transition is of the first-order type and upon chemical doping the transition is accompanied by large transfer of dynamical spectral weight from high to low energies. Several features of the Zhang-Rice bands[13] and the insulating state, which is shown to be of Mott-Hubbard type, are understandable within a strongly correlated scenario for d^9 layered oxides. In the moderately doped regime we find an anomalous spectral weight transfer characterized by the absence of new electronic states near the Fermi level, which is shown to be driven by strong correlations in a two-dimensional network. Our work supports the general picture proposed by Emery and by Varma *et al.*[12] that cuprate oxides belong to the class of systems where covalency and electron-electron interactions are strong, making it difficult to map the overall physical responses onto extended one-band Hubbard Hamiltonians.

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