Optical Weights and Waterfalls in Doped Charge Transfer Insulators: an LDA+DMFT Study of LSCO

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We use the Local Density Approximation in combination with the Dynamical Mean Field Theory to investigate intermediate energy properties of the copper oxides. We identify coherent and incoherent spectral features that result from doping a charge transfer insulator, namely quasiparticles, Zhang-Rice singlet band, and the upper and lower Hubbard bands. Angle resolving these features, we identify a waterfall like feature, between the quasiparticle part and the incoherent part of the Zhang-Rice band. We investigate the asymmetry between particle and hole doping. On the hole doped side, there is a very rapid transfer of spectral weight upon doping in the one particle spectra. The optical spectral weight increases superlinearly on the hole doped side in agreement with experiments.

Since their discovery, the high temperature superconductors continue to be a subject of intensive investigations. It is widely believed that strong correlations and many body effects are responsible for many of the peculiar properties of these materials. However, after many years of intensive studies, a comprehensive understanding of their electronic structure, even at intermediate energy scales, is lacking. The question of whether the symmetry of the on site correlations is sufficient to open the gap at half filling (Mott picture) or alternatively magnetism is required (Slater picture) is actively debated [1]. A vertical feature in the photoemission spectral intensity, commonly known as a waterfall, has recently been found in many compounds [2, 3], and it has been assigned to inherent spectral features that result from doping a charge transfer insulator, namely quasiparticles, and the optical weight, induced by doping the charge transfer insulator with a gap $\Delta_{pd} \approx 1.8 \text{eV}$ (green region). The number of electrons in the $d_{x^2-y^2}$ orbital ($n_d$) and in the $p_x$ orbitals ($n_p$) are also shown (right scale).

It is generally accepted that these materials contain copper-oxygen layers as a common element. Stoichiometric compounds such as La$_2$CuO$_4$, are antiferromagnetically ordered charge transfer insulators in the Zaaren-Sawatsky Allen [7, 8] classification scheme. Hence a minimal model of these materials contains two oxygen and one copper orbital per unit cell [9, 10]. When this model is doped with electrons, the low energy physics is believed to be closer to that of the Hubbard model. On the hole doped side, this reduction constructed by Zhang and Rice [11, 12] can be achieved in the limit that the charge transfer energy is much larger than the copper oxygen hybridization. However, there is no agreement on the precise region (in energy, and parameter space) where the reduction to a one band model is accurate.

In this letter, we use a realistic theoretical approach, i.e., the Local Density Approximation combined with the Dynamical Mean Field Theory (LDA+DMFT) [13], to study a typical cuprate compound La$_{2-x}$Sr$_x$CuO$_4$. The LDA calculation was done by PWSCF package [14], which employs a plane-wave basis set and ultrasoft pseudopotentials [15]. Downfolding to a three band model, containing copper $d_{x^2-y^2}$ and two oxygen $p_x$ orbitals was performed by the maximally localized Wannier functions (MLWF) method [16, 17]. We solve this model using Dynamical Mean Field Theory with an exact impurity solver [18].

We address the following questions. What are the spectral features that result from doping a charge transfer insulator? How are these spectral features distributed in momentum space? How does the quasiparticle residue and the optical weight, induced by doping the charge transfer insulator, vary with doping? We address the similarities and differences between our results and those that follow from a Hubbard model description.

Downfolding the LDA band structure of La$_2$CuO$_4$ results in the following three band Hamiltonian:

$$
\mathcal{H}_t = \sum_{ij\sigma,\langle\alpha,\beta\rangle(p_x,p_y),d_{x^2-y^2}} t_{ij}^{\alpha\beta} c_i^{\alpha\sigma} c_j^{\beta\sigma} + \epsilon_p \sum_{i\sigma} \hat{n}_{i\sigma} + \left(\epsilon_d - E_{dc}\right) \sum_{i\sigma} \hat{n}_{i d \sigma} $$

(1)

where $i$ and $j$ label the CuO$_2$ unit cells of the lattice, and $t_{ij}^{\alpha\beta}$ are the hopping matrix elements. $\epsilon_d$ and $\epsilon_p$ are the on-site energies of the $d$ and $p$ orbitals, respectively.

The charge transfer energy, $\Delta_{pd}$, between the copper...
and oxygen plays the role of an effective onsite repulsion $U$ in a Hubbard model picture, as seen for example in slave bosons mean-field studies [19].

The LDA downfolding procedure results in $\epsilon_d - \epsilon_p = 2.78$ eV. To this Hamiltonian, we add the onsite Coulomb repulsion $U$ on the $d_{x^2-y^2}$ orbital

$$\mathcal{H}_d = U_d \sum_i \tilde{n}_{id\uparrow} \tilde{n}_{id\downarrow}$$

where the value of $U_d = 8$ eV. The LDA+DMFT method, accounts for the correlations which are included in both LDA and DMFT by a double counting correction to the $d$-orbital energy, which we take to be fixed at $E_{dc} = 3.12$ eV for all dopings. We neglect the oxygen Coulomb repulsion $U_p$. Within single site DMFT, the copper-oxygen repulsion $V_{dp}$ is treated at the Hartree level, and hence it is included in the orbital energies of the $p$ and the $d$ orbitals.

The Green function of the three band model is given by:

$$G_k(i\omega_n) = (i\omega_n + \mu - H_k - \Sigma(i\omega_n))^{-1},$$

where $H_k$ is the Fourier transform of the $\mathcal{H}_d$ in Eq. (1) and is a $3 \times 3$ matrix. $\Sigma$ is the self-energy matrix being nonzero only in the $d$ orbital.

The self energy in Eq. (1) is obtained by solving an Anderson impurity model subject to the DMFT self-consistency condition:

$$\frac{1}{i\omega - E_{\text{imp}} - \Sigma(i\omega) - \Delta(i\omega)} = \frac{1}{N_k} \sum_{k \in BZ} G_{dd}^{\text{imp}}(i\omega),$$

where the sum runs on the first Brillouin Zone (BZ). In this work we use the continuous time quantum Monte Carlo impurity solver algorithm [18,21], which gives the self-energy functional $\Sigma[E_{\text{imp}}, \Delta]$ within the residual statistical error bars of the Monte Carlo algorithm [22]. Real frequency resolved quantities were obtained by analytic continuation (more details will be given elsewhere [22]) of the observables on the imaginary axis. We have crossed checked the analytic continuation using the OCA real frequency solver [23].

Equations (1) and (2) were studied previously in Refs. [24,25]. When $\gamma$ is large, there is a metal to charge transfer insulator transition at integer filling, as a function of the charge transfer energy $\epsilon_d - \epsilon_p$. For the set of realistic parameters considered in this letter, we find that the parent compound is a charge transfer insulator (see Fig. 1), with a hole density per Cu atom $\approx 85\%$ and a charge gap close to 1.8 eV. This places this material slightly above (but not very far) from the metal to charge transfer insulator transition point. This is demonstrated in Fig. 1, where the number of particles ($\delta$) as a function of chemical potential ($\mu$) exhibits a plateau in the interval $\mu = 14.2$ eV $-16$ eV. This figure also displays the partial occupancies, describing the relative distribution of the occupancies among copper and oxygen.

We have computed the spectral functions for both the parent and a doped compound. In the parent compound (not shown), we found four spectral peaks: i) the upper Hubbard band around $+2.5$ eV, ii) a singlet bound state of oxygen and copper known as the Zhang-Rice singlet just below the Fermi level, iii) the oxygen set of bands centered around $-7$ eV and iv) the lower Hubbard band at $-8$ eV. By hole doping (see Fig. 2b-right), the Zhang-Rice band is split into two peaks, the quasi-particle peak and the incoherent part which is associated with the lower Hubbard band in a single-band Hubbard model.

Figures 2a-left, and 2b show the momentum resolved...
The structure around \( \omega = 1.8 \) eV in both the paramagnetic and antiferromagnetic state. The optical gap in the parent compound is around \( \approx 1 \) eV and the position in the Brillouin zone where the abrupt change is observed (close to \((\pi/2, \pi/2)\)). While there are many interpretations of this feature \([2, 3, 4, 5, 6]\), we find that, a proper description of the waterfalls requires a multi-band model containing both oxygen and copper orbitals, as pointed out in Ref. \([1]\). The waterfall comes from the spectral gap between the incoherent part and the coherent (quasiparticle) part of the Zhang-Rice band. The latter is not present in the single site DMFT description of the parent compound, and our calculation in paramagnetic state of La\(_2\)CuO\(_4\) does not show splitting of the Zhang-Rice band into a low energy and a high energy part. We have found however, that when the anti-ferromagnetic broken symmetry state is considered for a parent compound, the splitting of the Zhang-Rice singlet is present, and the low energy part of the Zhang-Rice band is touching the Fermi level at \((\pi/2, \pi/2)\) momentum.

One of the most notable aspects of cuprate physics, is the rapid growth of the optical conductivity inside charge gap upon hole doping \([20]\). This was noted early on by Sawatzky and collaborators \([27]\). In order to tackle this issue, we computed the optical conductivity, given by:

\[
\sigma'(\omega) = \sum_{\sigma k} \frac{e^2}{\hbar c \pi} \int dx \frac{f(x - \omega) - f(x)}{\omega} \times \text{Tr} \left( \hat{\rho}_{k\sigma}(x - \omega) \hat{v}_k \hat{\rho}_{k\sigma}(x) \hat{v}_k \right) 
\]

(5)

Where \( c \) is the interlayer distance, the density matrix \( \hat{\rho} \) is defined by

\[
\hat{\rho}_{k\sigma}(x) = \frac{1}{2\pi i} \left( \hat{G}_{k\sigma}^{\dagger}(x) - \hat{G}_{k\sigma}(x) \right) 
\]

(6)

And the bare vertex is given by \( \hat{v}_k = d\hat{H}_k/dk_x \). Our results are displayed in Fig. 4. The optical gap in the parent compound is found to be 1.8 eV. To quantify the rate of the redistribution of optical spectral weight, we computed the effective electron number per Cu atom defined by

\[
N_{eff}^e = \frac{2m_e V}{\hbar c e^2} \int_0^\Lambda \sigma'(\omega) d\omega, 
\]

(7)

where \( m_e \) is the free electron mass, and \( V \) is the cell Volume containing one formula unit. \( N_{eff}^e \) is proportional
to the number of electrons involved in the optical excitations up to the cutoff Λ. Our results for \( N_{\text{eff}} \) are displayed in Fig. 3 and compared to experimental data taken from Ref. [20].

Notice that the spectral weight, contained in the region below the charge transfer gap of the parent compound, grows in a superlinear fashion. This is in agreement with experiments of Ref. [28] but is incompatible within a rigid band picture of doping either a band or a Mott insulator far from the Mott transition (as for example in the Hubbard model well above \( U_{c2} \)). Thus the optical spectral weight in the charge transfer insulator grows faster with doping than in the Mott insulator, where the linear growth of the spectral weight is expected.

The realistic three-band model within single site DMFT approach leads to a considerable asymmetry in the electron and hole doped side of the phase diagram. The superlinear behavior found in our calculation of the three band model is sufficient to explain the experimental findings, even though the correlations are strong enough to open a charge transfer gap in the parent compound even in the paramagnetic state.

We verified that this interesting particle hole asymmetry is present also in the quasiparticle residue \( Z = \left( 1 - \frac{\partial \Sigma(\omega)}{\partial \omega} \right)^{-1} \) and is shown in Fig. 3b. This is a one electron quantity that can be obtained directly from the imaginary axis data without the need to invoke analytic continuation, but still follows the same trend as \( N_{\text{eff}} \).

It is interesting to compare the asymmetry found here with the recent results of Ref. [29] on the Anderson lattice model. The authors found a much larger particle hole asymmetry compared to our results. Most likely this is due to a momentum independent hybridization function, which makes the Kondo scale in the hole doped side very small [29], and hard to reach with conventional QMC.

Phenomena in the underdoped region, such as the normal state pseudogap and the formation of fermi arcs, are not described by single site DMFT and require cluster extensions of the formalism [30]. However, single site DMFT is still expected to describe well intermediate energy phenomena, such as the distribution of the spectral weight upon doping the Mott/charge transfer insulator, which is the focus of our work. Momentum resolved quantities become more accurate in the overdoped region, where the self energy is more local.

For this reason, we have not considered here the details of the momentum dependent photoemission spectra at low doping, or the details of the frequency dependent optical conductivity, which are considerably influenced by cluster effects. We have rather focused on quantities such as \( N_{\text{eff}} \), which are less sensitive to cluster corrections and we rather presented the detailed photoemission spectra in the overdoped region, where actually the local approximation is valid [30].

In conclusion, we have carried out a realistic LDA+DMFT calculations accounting for the \( d_{x^2−y^2} \) and \( p_x \) orbitals of the three band model. The electron doped side is behaving mainly like the single-band Hubbard model. On the other hand, the hole doped side of the phase diagram is very different. a) We find a superlinear optical spectral weight transfer in agreement with experiments. b) On the spectral function, we find a spectral gap between the quasiparticle band and the incoherent Zhang Rice singlet band. This leads to a very abrupt and nearly vertical change in the spectral intensity in the nodal direction of the spectrum (waterfall), that ends up below 1 eV.

Our LDA+DMFT study support the view that the hole doped cuprates are above, but not very far from the metal charge transfer insulator transition in agreement with the conclusion of earlier slave boson studies [19].

It would be interesting to apply the same methodology to the electron doped cuprates which have a smaller charge transfer gap. These materials might have a charge transfer energy which lies below the critical value needed to sustain a paramagnetic insulator at integer filling, and hence might undergo a different metallization process upon doping, as suggested in Ref. [31].

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