Theory of oxygen $K$-edge x-ray absorption spectra of cuprates

Xin Wang$^1$, Luca de' Medici$^2$, and A. J. Millis$^1$

$^1$Department of Physics, Columbia University, 558 West 120th Street, New York, New York 10027, USA
$^2$Laboratoire de Physique des Solides, Université Paris-Sud, CNRS, UMR 8502, F-91405 Orsay Cedex, France

(Dated: March 10, 2010)

PACS numbers: 71.27.+a, 78.70.Dm, 74.25.Jb, 74.72.Gh

I. INTRODUCTION

The important structural unit of the high temperature copper-oxide superconductors is the "CuO$_2$ plane" and the important electronic orbitals are believed to be the Cu 3$d_{xy}$ and O 2$p_y$ states. High-$T_c$ superconductors are formed by doping (adding carriers to) an insulating parent compound. The nominal electronic configuration of the insulating parent compound is Cu 3$d^9$ (one hole in $d_{xy}$ band) O 2$p_y^6$ (oxygen p-band completely full), although of course Cu-O hybridization means that some fraction of the hole delocalizes onto the O. However, the strong correlations characteristic of the Cu $d$ orbitals implies that the energy required to add a second hole on the Cu site is very large, $U \sim 9$eV, so that at low doping levels, doped holes go primarily onto the oxygen site, but are strongly coupled via an exchange interaction to the holes on the Cu sites, forming "Zhang-Rice singlets".

While this picture is qualitative, being strictly valid only in the strong coupling limit and low doping limits, it has provided a useful guide for thinking about the materials. An important open question concerns the doping at which this picture breaks down.

Oxygen $K$-edge x-ray absorption spectra provides an interesting test of the Zhang-Rice picture, and more generally of our understanding of the three-band model. In these experiments absorption of an incident photon promotes an electron from the oxygen 1$s$ shell to an unoccupied oxygen orbital; if the photon energy is appropriately tuned, the final states are in the energy range of the O 2$p$ manifold and the spectrum reveals the energy distribution of the unoccupied O 2$p$ states (modified by the excitonic core-hole/excited state interactions). Experiments performed in the early 1990s on insulating and lightly-doped samples La$_{2-x}$Sr$_x$CuO$_{4+y}$ (LSCO) revealed a two-peak structure, with a higher energy peak visible in both insulating and hole-doped materials and a lower energy peak, visible only in hole-doped compounds. The integrated spectral weight of the lower energy feature was found to increase linearly with doping (at low hole-dopings) whereas the integrated spectral weight of the higher energy feature was found to decrease. For this reason the higher energy peak was interpreted as the "upper Hubbard band", while the lower energy feature was interpreted as the "Zhang-Rice band".

A recent experiment has extended the measurements to a wider range of compounds and in particular to a wider range of hole dopings. Fig. 1 summarizes the data, showing the recent measurements as "x"-shaped crosses with errorbars and the previous data as plus signs. A remarkable finding of the recent measurements is that the oxygen weight in the feature interpreted as the Zhang-Rice band saturates as doping is increased beyond the optimal doping value which maximizes the superconducting transition temperature $T_c$. Ref. 4 interpreted this finding as a breakdown of the Zhang-Rice singlet picture.

Motivated by these experiments, in this paper we use...
a more modern theoretical technique, namely single-site dynamical mean-field theory\textsuperscript{12,13} to compute the oxygen K-edge x-ray absorption spectra implied by the standard three-band copper-oxygen model of high-$T_c$ cuprate superconductors. The model contains the physics of Zhang-Rice singlets at low doping and strong correlations, but for higher doping or weaker correlations the behavior becomes band-like. We have examined the model both at strong coupling, where the state at half filling is a charge-transfer insulator\textsuperscript{6} and the physics at low doping is of Zhang-Rice singlets, and at weaker correlation strength, where antiferromagnetism is needed to make the model insulating at half filling and the appropriateness of the Zhang-Rice picture is less clear. We find that in both cases the model reproduces the low doping behavior but qualitatively fails to reproduce the experimental data at higher doping. We conclude that if the experiment indeed measures the oxygen density of states without other complicating effects, then the data indicate not just a failure of the Zhang-Rice model but a breakdown of the entire three-band model picture, with some additional orbital, not included in the three-band model, becoming important.

An additional consequence of our work is that by comparing the energies of the “Zhang-Rice band” and “upper Hubbard band” features to our calculations we are able to estimate the correlation strength of the materials. The comparison places the materials on the metallic side of the metal/charge-transfer-insulator phase diagram, in agreement with previous work.\textsuperscript{10,11}

The rest of this paper is organized as follows: Section \textsuperscript{II} describes the three-band model to be studied and the methods. In section \textsuperscript{III} we present the numerical results. Section \textsuperscript{IV} is a conclusion and discussion.

\section{Model and Methods}

The three-band Emery model considers Cu 3$d_{x^2−y^2}$ and O 2$p_x$ orbitals\textsuperscript{12,13} which hybridize via a copper-oxygen hopping $t_{pd}$. We shall also consider oxygen-oxygen hoppings, adopting the form implied by the considerations of Ref. \textsuperscript{14}. The model exhibits both a low-doping antiferromagnetic phase and a high-doping paramagnetic phase but because the experimentally interesting behavior occurs at high dopings, we restrict our attention in the paramagnetic phase. We distinguish the oxygen sites displaced from the Cu in the $x$ and $y$ directions, adopt the basis $|ψ\rangle = (d_{kσ}, p_{x,kσ}, p_{y,kσ})$, introduce the copper-oxygen hopping $t_{pd} = 1.6eV$ and oxygen-oxygen hopping $t_{pp}$ in the form proposed by Andersen\textsuperscript{14} we compare $t_{pp} = 1.1eV$ and $t_{pp} = 0.11$ The interaction part of the Hamiltonian is

$$
H_{int} = U \sum_i n_{i↑} n_{i↓},
$$

and in the calculation presented here we take $U = 9eV$ (the precise value of $U$ is not important as long as it is larger than about 5eV). The band theoretic part of the Hamiltonian may be represented as a $3 \times 3$ matrix:

$$
H_{3\text{band}} = \begin{pmatrix}
\varepsilon_d & 2it_{pd} \sin \frac{k_x}{2} & 2it_{pd} \sin \frac{k_y}{2} \\
-2it_{pd} \sin \frac{k_x}{2} & \varepsilon_p + 2t_{pp} (\cos k_x - 1) & 4t_{pp} \sin \frac{k_x}{2} \sin \frac{k_y}{2} \\
-2it_{pd} \sin \frac{k_y}{2} & 4t_{pp} \sin \frac{k_x}{2} \sin \frac{k_y}{2} & \varepsilon_p + 2t_{pp} (\cos k_y - 1)
\end{pmatrix}.
$$

The model has two important parameters: $U$ and $\Delta = \varepsilon_p - \varepsilon_d$. The physically relevant case is large $U$, in which case the model is in the charge-transfer regime\textsuperscript{6} and the physics is controlled by the ratio of $\Delta$ to the copper-oxygen hopping $t_{pd}$. At “half filling” (one hole in the $d$-$p$ complex) the single-site dynamical mean-field approximation predicts that the model exhibits a paramagnetic insulating phase for small $\Delta$ whereas the paramagnetic phase is metallic at large $\Delta$. In previous work\textsuperscript{10,11} we have determined that for $U = 9eV$, $\Delta = 2eV$ is on the insulating side, but not far from the metal-insulator phase boundary, whereas $\Delta = 4eV$ lies on the metallic side of the phase diagram, but also not far from the boundary. The correct value of $\Delta$ for the cuprates is controversial\textsuperscript{10}, we therefore consider $\Delta$-values corresponding both to paramagnetic metal and to paramagnetic insulating phases at half filling.

The model is solved using the single-site dynamical mean-field approximation\textsuperscript{12,13} in which the key approximation is a momentum-independent self-energy:

$$
\Sigma(z, k) \rightarrow \Sigma(z) = \begin{pmatrix}
\Sigma(z) & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix},
$$

where $z$ indicates real or Matsubara frequencies. The Green’s function is

$$
G(z, k) = (z 1 + \mu - \Sigma(z) - H_{3\text{band}})^{-1},
$$

and the spectral functions (density of states) of $d$ and $p$ orbitals are obtained from the imaginary part of the diagonal elements of the Green’s function matrix.

We employ two impurity solvers: Exact Diagonalizations (ED)\textsuperscript{12,13} and the hybridization-expansion
continuous-time quantum Monte Carlo method (QMC). Because the two methods involve different approximations, comparison of the results helps confirm the accuracy of the methods. Analytic continuation of the QMC data is performed using the method described in Ref. 18. The model has been previously studied. At strong correlations and low dopings the approximation reveals the “Zhang-Rice singlet” behavior with doped holes residing on the oxygen but strongly antiferromagnetically coupled to spins on the copper sites. As the doping is increased or the effective correlation strength decreased, the behavior reverts to moderately-correlated band behavior and a Zhang-Rice picture becomes inappropriate.

From the calculation we obtain the electron spectral function \( A(\omega) = \text{Im} G(\omega) \) which we use to model the X-ray absorption experiment. As noted in Ref. 5, the X-ray absorption cross section is not simply proportional to the product of a matrix element and electron spectral function because the hole in the oxygen 1s core state interacts with the excited electron. We assume, following Ref. 3 that this effect provides a constant (Hartree) shift on the lineshape and on spectral weight. Therefore the x-ray absorption spectrum is given by

\[
B(\omega) = C \cdot A_{oxy}(\omega - \omega_0)[1 - f(\omega - \omega_0)],
\]

where \( A_{oxy}(\omega) \) is the calculated electron spectral function, projected onto the oxygen site, \([1 - f(\omega)]\) is the complement of the Fermi function, restricting the result to unoccupied states, \( C \) encodes the matrix element and \( \omega_0 \) is the energy difference between the final and initial state, including the effect of the excitonic interaction between the core hole and the excited electron. In our calculations we set \( \omega_0 \) for 0.1 hole doping case such that the upper Hubbard band peaks at 530.2\( eV \). The \( \omega_0 \) for other doping values are computed by adding a Hartree shift to the 0.1 hole-doped case, using the Hamiltonian and parameters described by Ref. 3 with the calculated occupation numbers.

### III. RESULTS

Fig. 2 shows the doping dependence of the electron spectral functions, calculated as described above and projected onto the oxygen orbitals, for \( \Delta = 2eV \) (insulator in undoped case) and 4\( eV \) (metal in undoped case), in absence of \( t_{pp} \). Results obtained from both analytic continuation of QMC and ED impurity solvers are shown; the close correspondence between the results of the two methods indicates that the solution of the model is reliable.

Two features are evident in the calculated spectra: a higher energy feature which corresponds to the upper Hubbard band (its weight is small because this band is comprised mainly of \( d \)-states so it has a small projection onto the oxygen states) and a lower energy feature corresponding to the Zhang-Rice band. The difference in energy between the two features is an estimate of the correlation gap in the system. One sees that the gap size is about 4\( eV \) in the \( \Delta = 2eV \) (insulator in undoped case) case, and around 2\( eV \) in \( \Delta = 4eV \) (metal in undoped case) case, and we expect the gap will further shrink if we go deeper in the metallic phase of the paramagnetic phase diagram. Experiments show that the observed gap between the two peaks is \( \lesssim \Delta \approx 4eV \), which is more consistent with the \( \Delta = 4eV \) results, in agreement with our previously published papers, placing the cuprates on the paramagnetic metal side of the phase diagram, so that the correlations are intermediate rather than strong.

Fig. 3 shows results for the case \( t_{pp} = 1.1eV \) obtained from analytic continuation of the QMC data for the un-

---

**FIG. 2:** Unoccupied portion of three-band model many-body density of states, projected onto oxygen orbitals, calculated as described in the text for dopings \( x \) indicated on figure using both analytical continuation of QMC [panels (a)] and ED [panels (b)] impurity solvers for two values of charge transfer gap \( \Delta; \Delta = 4eV \) (upper panels) corresponding to half filled paramagnetic metal and \( \Delta = 2eV \) (lower panels) corresponding to paramagnetic insulating phase at half filling. Parameters: \( U = 9eV \), \( t_{pd} = 1.6eV \) and temperature \( T = 0.1eV \).
occupied oxygen density of states. The similarity of these curves to the results shown in Fig. 2 indicates that oxygen-oxygen hopping does not have an important effect on the results.

We have integrated the area in the lower energy feature shown in Figs. 2 and 3 normalized the results to the value at hole doping 0.22 and have plotted the resulting spectral weight as diamonds etc. in Fig. 1. For both values of $\Delta$ the integrated spectral weight is found to increase linearly with doping over a wide doping range. Differences between the $\Delta = 2eV$ case (strong correlation, doped charge-transfer insulator) and the $\Delta = 4eV$ case (intermediate correlation, charge-transfer metal) appear only at low dopings $x \lesssim 0.11$. For completeness we present also in Fig. 4 the integrated oxygen weight in the upper Hubbard band. We see that the spectral weight of the Zhang-Rice band continue to increase at the overdoped region, while the weight of the upper Hubbard band decreases. Both the weight in the Zhang-Rice band and the weight in the upper Hubbard band vary smoothly with doping for all parameters. The sharp break in the data is not observed in the calculation for any choice of parameters. We therefore conclude that the experimental paper understated the significance of the results: the data indicate not just a breakdown of the Zhang-Rice picture, but a failure of the three-band model itself.

### IV. CONCLUSION

In this paper we have used single-site dynamical mean-field theory to study the Emery three-band copper-oxide model related to the cuprates. We have calculated the doping dependence of the intensity of oxygen $K$-edge x-ray absorption spectra. At high doping, our calculations do not reproduce the results of a recent experiment (Ref. 4). This implies a breakdown of “Zhang-Rice singlet” approximation and even a failure of the three-band model picture.

We may speculate on the reason for the failure of the three-band model in the overdoped regime. One possibility is that the electronic structure changes in such a way that new degrees of freedom (beyond the conventionally studied copper $d_{x^2-y^2}$ and oxygen $p_x$) states become important (for example other states in the $d$-multiplet or apical oxygen states) providing a new channel for adding doped holes. An alternative possibility might be that for some reason the arguments relating the experimental measurement to the oxygen density of states break down, or that there is an unusual change in the matrix element. Such a change would presumably be related to a change in the electronic structure. A third possibility is that additional physics, such as a $U_{pp}$ on the oxygen states, begins to play a role; however it is not clear why this would lead to a sudden change in doping dependence. The effect of additional orbitals is presently under investigation.

### Acknowledgements

XW and AJM are financially supported by NSF-DMR-0705847 and LdM by Program ANR-09-RPD0C-019-01 and RTRA Triangle de la Physique. Part of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.
1. F. Mila, F. C. Zhang, and T. M. Rice, Physica C 153-155, 1221 (1988).
2. M. A. van Veenendaal, G. A. Sawatzky, and W. A. Groen, Phys. Rev. B 49, 1407 (1994).
3. F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
4. C. T. Chen, F. Sette, Y. Ma, M. S. Hybertsen, E. B. Stechel, W. M. C. Foulkes, M. Schlüter, S-W. Cheong, A. S. Cooper, L. W. Rupp, Jr., B. Batlogg, Y. L. Soo, Z. H. Ming, A. Krol, and Y. H. Kao, Phys. Rev. Lett. 66, 104 (1991).
5. M. S. Hybertsen, E. B. Stechel, W. M. C. Foulkes, and M. Schlüter, Phys. Rev. B 45, 10032 (1992).
6. D. C. Peets, D. G. Hawthorn, K. M. Shen, Y.-J. Kim, D. S. Ellis, H. Zhang, S. Komiya, Y. Ando, G. A. Sawatzky, R. Liang, D. A. Bonn, and W. N. Hardy, Phys. Rev. Lett. 103, 087402 (2009).
7. A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. 68, 13 (1996).
8. G. Kotliar, S. Y. Savrasov, K. Haule, V. S. Oudovenko, O. Parcollet, and C. A. Marianetti, Rev. Mod. Phys. 78, 865 (2006).
9. J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. 55, 418 (1985).
10. A. Comanac, L. de’ Medici, M. Capone, and A. J. Millis, Nat. Phys. 4, 287 (2008).
11. L. de’ Medici, X. Wang, M. Capone, and A. J. Millis, Phys. Rev. B 80, 054501 (2009).
12. V. J. Emery, Phys. Rev. Lett. 58, 2794 (1987).
13. C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. 62, 681 (1987).
14. O. K. Andersen, A. I. Liechtenstein, O. Jepsen, and F. Paulsen, J. Phys. Chem. Solids 56, 1573 (1995).
15. M. Caffarel and W. Krauth, Phys. Rev. Lett. 72, 1545 (1994).
16. M. Capone, M. Civelli, S. S. Kancharla, C. Castellani, and G. Kotliar, Phys. Rev. B 69, 195105 (2004).
17. P. Werner, A. Comanac, L. de’ Medici, M. Troyer, and A. J. Millis, Phys. Rev. Lett. 97, 076405 (2006).
18. X. Wang, E. Gull, L. de’ Medici, M. Capone, and A. J. Millis, Phys. Rev. B 80, 045101 (2009).
19. G. Dopf, A. Maramatsu, and W. Hanke, Phys. Rev. Lett. 68, 353 (1992).
20. A. Georges, B. G. Kotliar, and W. Krauth, Z. Phys. B 92, 313 (1993).
21. M.B. Zölfl, T. Maier, T. Pruschke and J. Keller, European Physical Journal B 13, 47 (2000).
22. A. Marzlin, M. Jarrell, Th. Maier, and G.A. Sawatzky, Phys. Rev. B 71, 134527 (2005).
23. C. Weber, K. Haule and G. Kotliar, Phys. Rev. B 78, 134519 (2008).
24. L. Craco, Phys. Rev. B 79, 085123 (2009).