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

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The dynamical mean-field theory of the three-band model of copper-oxide superconductors is used to calculate the doping dependence of the intensity of the oxygen *K* edge x-ray absorption spectra of high-T_c copper-oxide superconductors. The model is found not to reproduce the results of a recent experiment, suggesting that at sufficiently high doping the physics beyond the conventional three-band model becomes important.

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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 $3d_{x^2-y^2}$ and O $2p_\sigma$ 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 $3d^9$ (one hole in $d_{x^2-y^2}$ band) O $2p^6$ (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 (Refs. 1 and 2) 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."[3] 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 $2p$ manifold and the spectrum reveals the energy distribution of the unoccupied O $2p$ states (modified by the excitonic core-hole/excited-state interactions). Experiments performed in the early 1990s (Ref. 4) on insulating and lightly doped samples $La_{2-x}Sr_xCuO_{4\pm\delta}$ (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.[4,5] 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[6] has extended the measurements to a wider range of compounds and, in particular, to a wider range of hole dopings. Figure 1 summarizes the data, showing the recent measurements as "x"-shaped crosses with error bars and the previous data[4] 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. Reference 6 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[7,8] 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

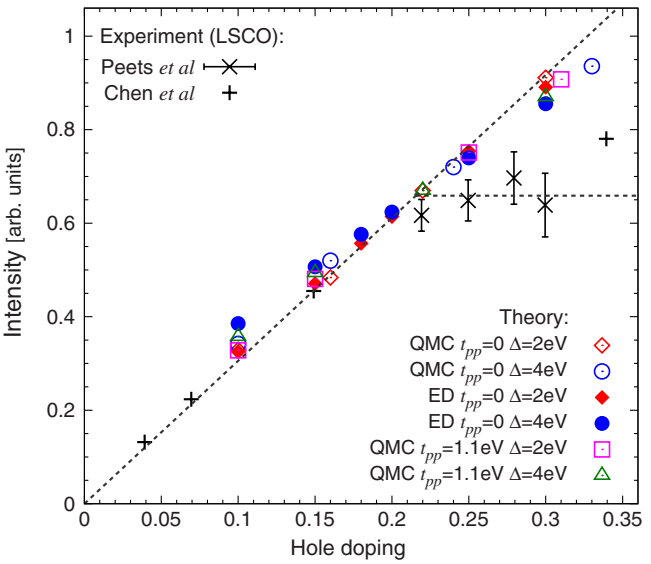

FIG. 1. (Color online) Relative intensity of the peak associated with the Zhang-Rice band of O *K* edge x-ray absorption spectra vs doping. The plus sign shows experiments on LSCO by Chen *et al.* (Ref. 4) and the x-shaped sign shows experiments on LSCO by Peets *et al.* (Ref. 6). The diamonds, circles, squares, and triangles are theoretically calculated integrated spectral weight of unoccupied oxygen states, normalized such that their values at 0.22 hole doping are the same. Dashed lines are only guides to eyes. Parameters: $U=9$ eV, $t_{pd}=1.6$ eV, $T=0.1$ eV, t_{pp}, and $\Delta=\varepsilon_p-\varepsilon_d$ as shown in the legends.

low doping and strong correlations but for higher doping or weaker correlations the behavior becomes bandlike. We have examined the model both at strong coupling, where the state at half filling is a charge-transfer insulator[9] 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.[6] 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.[10,11]

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

II. MODEL AND METHODS

The three-band Emery model considers Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals,[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. 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 $|\psi\rangle=(d_{k\sigma},p_{x,k\sigma},p_{y,k\sigma})$, introduce the copper-oxygen hopping $t_{pd}=1.6$ eV and oxygen-oxygen hopping t_{pp} in the form proposed by Andersen;[14] we compare $t_{pp}=1.1$ eV and $t_{pp}=0$.[11] The interaction part of the Hamiltonian is

$$H_{\rm int}=U\sum_i n_{d\uparrow}n_{d\downarrow} \tag{1}$$

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

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

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[9] and the physics is controlled by the ratio of Δ 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 Δ whereas the paramagnetic phase is metallic at large Δ. In previous work[11] we have determined that for $U=9$ eV, $\Delta=2$ eV is on the insulating side, but not far from the metal-insulator phase boundary, whereas $\Delta=4$ eV lies on the metallic side of the phase diagram, but also not far from the boundary. The correct value of Δ for the cuprates is controversial;[10] we therefore consider Δ 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,[7,8] in which the key approximation is a momentum-independent self-energy,

$$\mathbf{\Sigma}(z,\mathbf{k})\to\mathbf{\Sigma}(z)=\begin{pmatrix}\Sigma(z) & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 0\end{pmatrix}, \tag{3}$$

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

$$\mathbf{G}(z,\mathbf{k})=[(z+\mu)\mathbf{1}-\mathbf{\Sigma}(z)-\mathbf{H}_{\rm 3band}]^{-1}, \tag{4}$$

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 diagonalization (ED) (Refs. 15 and 16) and the hybridization-expansion continuous-time quantum Monte Carlo (QMC) method.[17] 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

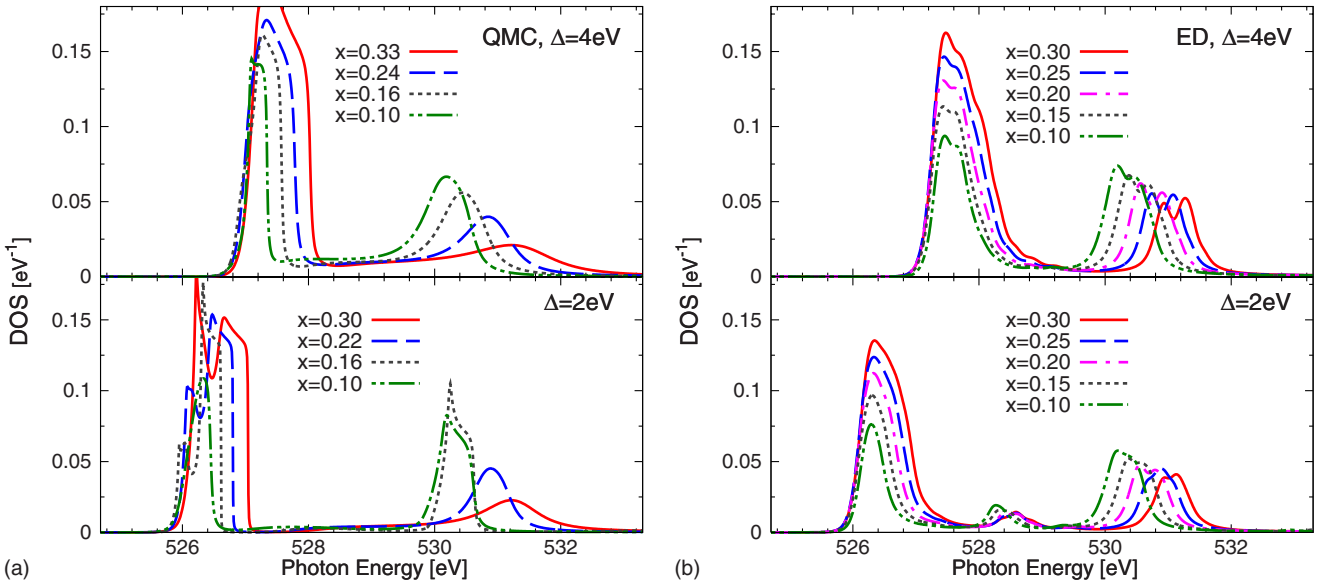

FIG. 2. (Color online) Unoccupied portion of three-band model many-body density of states, projected onto oxygen orbitals, calculated as described in the text for dopings x indicated in the figure using both analytic continuation of QMC [panels (a)] and ED [panels (b)] impurity solvers for two values of charge transfer gap Δ; $\Delta=4$ eV (upper panels) corresponding to half-filled paramagnetic metal and $\Delta=2$ eV (lower panels) corresponding to paramagnetic insulating phase at half filling. Parameters: $U=9$ eV, $t_{pp}=0$, $t_{pd}=1.6$ eV, and temperature $T=0.1$ eV.

has been previously studied:[11,19–24] 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 $A(\omega)=\mathrm{Im}\,G(\omega)$ 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. 5 that this effect provides a constant (Hartree) shift of the spectrum, and, in particular, has a negligible effect on the line shape and on spectral weight. Therefore the x-ray absorption spectrum is given by

$$B(\omega) = CA_{oxy}(\omega-\omega_0)[1-f(\omega-\omega_0)], \tag{5}$$

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 ω_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 ω_0 for 0.1 hole-doping case such that the upper Hubbard band peaks at 530.2 eV.[4] The ω_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. 5 with the calculated occupation numbers.

III. RESULTS

Figure 2 shows the doping dependence of the electron spectral functions, calculated as described above and projected onto the oxygen orbitals, for $\Delta=2$ eV (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 $\Delta=2$ eV (insulator in undoped case) case, and around 2 eV in $\Delta=4$ eV (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[4,6] show that the observed gap between the two peaks is $\lesssim 2$ eV, which is more consistent with the $\Delta=4$ eV results, in agreement with our previously published papers[10,11] placing the cuprates on the paramagnetic metal side of the phase diagram, so that the correlations are intermediate rather than strong.

Figure 3 shows results for the case $t_{pp}=1.1$ eV obtained from analytic continuation of the QMC data for the unoccupied 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

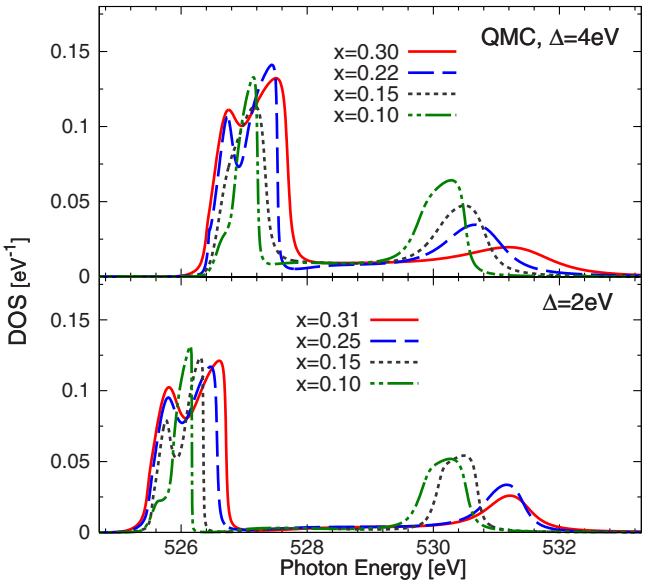

FIG. 3. (Color online) Calculated unoccupied oxygen density of states computed as a function of doping as described in the text for nonvanishing oxygen-oxygen hopping $t_{pp}=1.1$ eV by analytic continuation of QMC calculations. Other parameters: $U=9$ eV, $t_{pd}=1.6$ eV, and temperature $T=0.1$ eV.

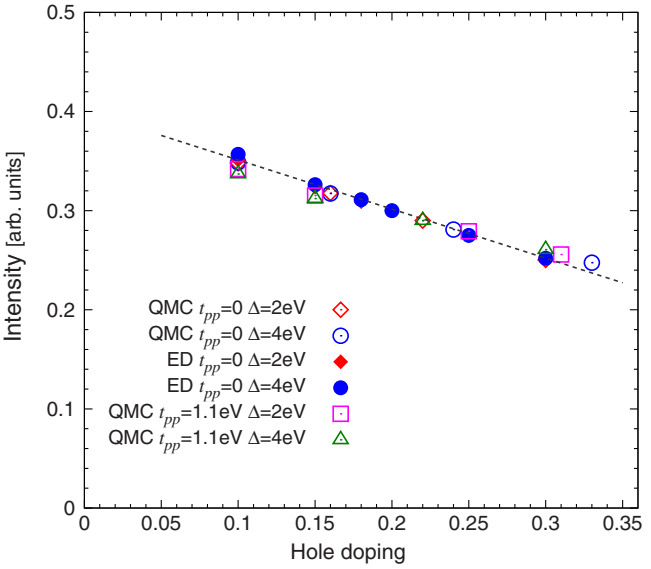

FIG. 4. (Color online) Calculated relative intensity of the peak associated with the upper Hubbard band of O K edge x-ray absorption spectra vs doping. The results are normalized such that their values at 0.22 hole doping are the same. The dashed line is only guide to eyes. Parameters: $U=9$ eV, $t_{pd}=1.6$ eV, $T=0.1$ eV, t_{pp}, and $\Delta=\varepsilon_p-\varepsilon_d$ as shown in the legends.

hole doping 0.22 and have plotted the resulting spectral weight as diamonds, etc., in Fig. 1. For both values of Δ the integrated spectral weight is found to increase linearly with doping over a wide doping range. Differences between the $\Delta=2$ eV case (strong correlation, doped charge-transfer insulator) and the $\Delta=4$ eV 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 does not reproduce the results of a recent experiment (Ref. 6). This implies a breakdown of Zhang-Rice singlet approximation and even a failure of the entire 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_σ) 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.

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