Electronic correlations and satellites in superconducting oxides

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The satellite observed at binding energy of 12–13 eV below the Fermi level in the high-T_c oxide superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ is viewed as originating from a state with two holes bound at the same Cu site. As in the case of Ni metal, the satellite is caused by an intra-d-shell shakeup process into a Cu $3d^8$ final state and its intensity is enhanced at resonance because of a super-Koster-Kronig transition. Based on the t-matrix approach for the hole self-energy, we study the effect of electronic correlations on the one-electron band structure. We examine the position of the satellite and find a large Coulomb interaction energy of ~ 5 eV at the Cu site when the experimental satellite position is duplicated by the theory. Since this energy is comparable with the $3d$ bandwidth, the two-hole bound state is a high-energy excitation. This indicates that in the ground state a creation of two holes at the Cu site is unlikely and thus holes are formed at the O sites when Sr is substituted for La in La_2CuO_4 and when the oxidation is increased in $YBa_2Cu_3O_{7-\delta}$.

I. INTRODUCTION

The observations of high-temperature superconductivity in the copper oxides $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ have led to intense experimental and theoretical activity.[1] Although many mechanisms giving rise to pairing have been suggested,[1–6] the dominant mechanism has not yet been identified and thus a clear understanding of the superconductivity remains open and an important issue. In contrast to conventional high-T_c superconductors below 23 K, the results obtained from the photoemission[7–14] and Auger spectroscopies[15,16] have demonstrated strong electronic correlation effects in the oxide superconductors. Strong on-site correlations are also indicated by the observation of antiferromagnetism in these materials.[17] For Y-based oxides, there have been critical experimental and theoretical results that argue against the conventional phonon mechanism; small O-isotope effects[18,19] were observed and calculated electron-phonon couplings[20] were found to yield T_c's of only 30–40 K which are smaller than the observed temperature of 90 K. In conjunction with these facts, some of the nonconventional superconducting mechanisms[2–4,6] proposed are purely electronic in origin based on Coulomb correlations between Cu $3d$ electrons. Therefore it is important to study the effects of electronic correlation on the one-electron band structure.

Strong intra-atomic electron-electron correlations in a material are generally signaled by the existence of satellites in its resonant photoemission spectra. Resonant photoemission was first observed in Ni metal by Guillot *et al.*[21] and the resonant satellite they observed was explained by Penn[22] as arising from two $3d$ holes bound on the same site. Similar resonant features were also seen in other materials including Cu (Ref. 23) with the closed $3d$ shells, transition metal oxides such as NiO (Ref. 24) and CuO,[25] and copper dihalides.[26,27]

Recent resonant photoemission spectra[7–16] of the superconducting oxides showed the existence of satellites in these materials. In contrast to Ni, the satellites were found to be positioned below the valence bands indicating strong electronic correlations at the Cu sites. Some of the photoemission data[9,14] also suggested the possibility of strong correlations at O sites. These satellite features are not found in one-electron band theories.[28–33] Although the differences between the band-structure results and the photoemission measurements for the binding energies of the Cu $3d$– and O $2p$–derived bands and the spectral density at the Fermi level may arise from surface contamination of the data,[34] the observed satellite is considered to be a true bulk property. If the photoemission data are reliable, the observed shift of the main band peak with respect to the Fermi level may be the result of the omission of self-energy effects in the local density calculation.

Our approach in the present work is to view the satellites found in the oxide superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ as arising from correlations among Cu $3d$ electrons. We demonstrate that the satellite at about 12–13 eV results from the transition to the two-hole bound state at the Cu site with the intra-$3d$-shell Auger spectra accompanied by electron photoexcitation. This behavior in oxides is similar to the cases of Ni metal and

other transition metal oxides. Using the t-matrix approach[22,35] to describe multiple-hole scatterings, we calculate the spectral function of the hole state and compare it with the photoemission results. The satellite feature is well reproduced and the on-site Cu correlation energy as determined from the position of the satellite is comparable with other estimates. We also discuss the connection between the satellite and the main valence bands and consider several differences found between one-electron band features and the experimental data. Finally, this paper will be organized as follows: the theoretical method is described in Sec. II, the results of the calculations are given and discussed in Sec. III, and Sec. IV summarizes our work.

II. THEORETICAL METHODS

The formalism to describe strong Coulomb correlation between holes at the same site is based on the degenerate Hubbard Hamiltonian

$$H=\sum_{k,n,\sigma}\varepsilon_{kn}C^{\dagger}_{kn\sigma}C_{kn\sigma} +\tfrac{1}{2}\sum_{i,n,n',\sigma,\sigma'}U_i(1-\delta_{nn'}\delta_{\sigma\sigma'})n_{i,n\sigma}n_{i,n'\sigma'} , \quad (1)$$

where ε_{kn} is the band energy of an electron with a Bloch state kn that is a linear combination of atomic states, i denotes the Cu and O sites, and $C^{+}_{kn\sigma}$ and $C_{kn\sigma}$ represent the creation and destruction operators, respectively, of an electron with a state $kn\sigma$. In the second term of Eq. (1), U_i is the intra-atomic Coulomb matrix for holes at the site i represented by either on-site d-d or p-p repulsive interaction. The intersite interactions U_{ij} $(i\neq j)$ between Cu and O atoms are not considered here. The same formulation was previously used to study the satellites in Ni metal.[22,35] The Hamiltonian given in Eq. (1) is assumed to describe the Cu $3d$ and O $2p$ electrons in La- and Y-based oxides. In the ground state, the configurations for Cu and O are assumed to be $Cu^{1+}(3d^{10})$ and $O^{2-}(2p^6)$, respectively, where both the $3d$ and $2p$ bands are filled.

To model the energy spectra for the photoexcited hole, we assume that holes in the Cu $3d$ or O $2p$ bands are strongly correlated and their self-energies are caused by hole-hole Coulomb interactions at the same site. In general, the hole self-energy also includes contributions from electron-hole interactions and higher-order processes.[35] However, for simplicity these correction terms are not considered here because they are not essential in determining general features of the spectra. Since the inverse photoemission spectra showed no pronounced peaks which are related to the Cu $3d$ and O $2p$ states,[10,15] it is reasonable to neglect electron-electron scattering in the self-energy for the electron states above the Fermi level E_F.

In the following we will focus on the hole self-energy and the valence-band spectra. For a partially filled band, a photoexcited hole can scatter to another hole state accompanied by an electron-hole pair excitation through an Auger event within the same band. In this case, two d (or p) holes multiply scatter at the same Cu (or O) site and this multiple scattering can create a bound two-hole state. The multiple interactions were shown to be described either within a t-matrix approximation[22,35] or a perturbation theory[36] in U_i/W_i where W_i is the bandwidth for the atom of type i. The satellites observed in the superconducting oxides are below the valence bands indicating that the atomic limit is appropriate where U_i is comparable to W_i. Thus, the use of the second-order perturbation approach is not appropriate. In the t-matrix approach, as shown diagrammatically in Fig. 1(a), t satisfies the integral equation

$$t=v+vG^{(2)}t , \quad (2)$$

where v denotes the Coulomb interaction and $G^{(2)}$ is the two-hole Green function. The one-hole Green function $G^{(1)}$ is given by the Dyson equation

$$G^{(1)}=g+g\Sigma G^{(1)} , \quad (3)$$

where g is the bare-hole Green function and Σ is the hole self-energy. Figures 1(b) and 1(c) show $G^{(1)}$ and Σ diagramatically.

For the Hubbard Hamiltonian with an intra-atomic Coulomb interaction of strength U_i, $G_i^{(2)}$ for holes at a site i is approximated by its average over momentum and spin, as justified for the case of Ni,[22]

$$G_i^{(2)}(\xi)=\int d\varepsilon\int d\varepsilon'\frac{f(\varepsilon)f(\varepsilon')\rho_0^i(\varepsilon)\rho_\sigma^i(\varepsilon')}{\xi-\varepsilon-\varepsilon'-i\delta} , \quad (4)$$

where ρ_0^i is the normalized density of states for holes at a site i. Then, Eqs. (1) and (2) yield

$$t_i(\xi)=\frac{U_i}{1+U_iG_i^{(2)}(\xi)} \quad (5)$$

and the hole self-energy Σ_i at the site i is given by

$$\Sigma_i(\omega)=-\sum_{k,n}[1-f(\varepsilon_{kn})]t_i(\omega+\varepsilon_{kn}) . \quad (6)$$

For large values of U_i, the t matrix in Eq. (5) has a pole which determines the position of the satellite. Since the momentum dependence in $G^{(2)}$ is negligible, t produces little dispersion of the satellite and thus the satellite has a sharp peak at approximately the same energy as the pole in the t matrix. From Eq. (6), the hole self-energy is essentially proportional to the number of empty states in the band. The t-matrix approach is exact in the limit of a small number of unoccupied states.[37]

The spectral density for the hole state kn at the site i is

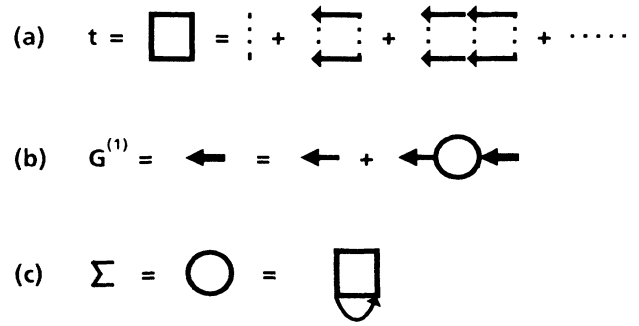

FIG. 1. Diagrams represent (a) the t matrix, (b) the two-hole Green function, and (c) the hole self-energy.

represented by the imaginary part of the one-particle Green function

$$A_i(k,n;\omega)=\frac{1}{\pi}\mathrm{Im}(G_i^{(1)}) =\frac{1}{\pi}\mathrm{Im}\left[\frac{1}{\omega-\varepsilon_{kn}-\Sigma_i(k,n;\omega)}\right] \quad (7)$$

and the total photoemission spectra $n(\omega)$ is given by summing over all types of atom and the states (k,n):

$$n(\omega)=\sum_{i,k,n} A_i(k,n;\omega) . \quad (8)$$

Because of the local approximation for t through Eq. (4), Σ_i in Eq. (7) is independent of kn and the summation over kn in Eq. (8) can be replaced by an integration over energy:

$$n(\omega)=\frac{1}{\pi}\sum_i \int d\omega' \, n_0(\omega')\mathrm{Im}\left[\frac{1}{\omega-\omega'-\Sigma_i(\omega)}\right] , \quad (9)$$

where $n_0(\omega)$ is the density of states without self-energy corrections.

In the large-U_i limit, a two-hole spectrum is easily derived for a simple model where all band energies are approximated by a single band $\varepsilon\approx\varepsilon_d$. In this case, $G_i^{(2)}$ in Eq. (4) is replaced by

$$G_i^{(2)}(\xi)\approx\frac{1}{\xi-2\varepsilon_d-i\delta} \quad (10)$$

and $\mathrm{Im}(t_i)$ becomes nonzero at an energy ξ_0 where $1+U_i\mathrm{Re}[G_i^{(2)}(\xi_0)]=0$. At the energy ξ_0, holes are at the same lattice site and experience a Coulomb repulsion of strength U_i. This simple model gives two peaks in the spectra which are separated by U_i; the peaks lie at energies of ε_d-U_i and ε_d. Here a new peak at ε_d-U_i corresponds to the satellite and its spectral weight compared to the main peak is roughly proportional to the number of unoccupied states above the Fermi level. The spectral density is actually removed from the band to the satellite because of the self-energy corrections and thus the valence-band feature is modified as discussed for Ni.[22,35,38]

III. RESULTS AND DISCUSSION

The electronic structures of La_2CuO_4 and $YBa_2Cu_3O_{6.5}$ have been studied by several theoretical groups.[28–33] Although the crystal structures are found to be different in these materials, they have similar two-dimensional crystal planes in which Cu $3d$-and O $2p$-derived orbitals are strongly hybridized.[1] The two dimensionality of this plane yields the following character for the electronic states; the Cu $3d_{x^2-y^2}$–O $2p_{x,y}$ antibonding states are found to be half-filled while the bonding states are occupied. Because of the Cu $3d$ and O $2p$ states in the energy bands near the Fermi level, the Cu $3d$ bands can accommodate a hole. The nonbonding states which are composed of the Cu $3d_{z^2}$ and O $2p_z$ orbitals are found at energies ranging from 1 to 4 eV below the Fermi level producing the main peak in the valence bands. It has been suggested that the Cu-O planes with the half-filled bands have a nearly perfect nesting of the Fermi surface which yields a high density of states at E_F and the resulting charge-density wave instability induces a semiconducting transition. The one-electron band structures, however, do not show the satellite features observed in the superconducting oxides.

The satellites seen in resonant photoemission spectroscopy generally indicate the existence of strong correlations and thus localized states. Far from resonances, two holes at the same site experience strong Coulomb repulsive interactions through an intra-d-shell Auger transition accompanied by the photoexcitation while at resonance, a $3p$ to $3d$ photoexcitation with an Auger effect leads to a resonant satellite. Such an intra-d-shell shakeup process occurs within the open $3d$ shells and has also been identified in Auger spectra.[39,40] Similar shakeup processes are observed for transition metal oxides CuO and NiO (Refs. 24 and 25) and copper dihalides[26,27] with unoccupied $3d$ bands. For Cu, however, a weak satellite is seen.[23] In this case, the $3d$ states are full and thus it was suggested that a different shakeup process such as a transition from the $3d$ to the $4s,p$ state gives rise to the satellite. A large amount of theoretical and experimental work has been reviewed by Davis.[41]

For La- and Y-based oxides, at photon energies corresponding to the Cu $3p$ threshold, resonant satellite features were observed at a binding energy around 12–13 eV below E_F.[7–11,13–16] The results of the photoemission spectroscopy indicated that these satellites are similar to those found in CuO; at resonance, three multiplets in the satellite were found as in the case of CuO.[25] The binding energies for the satellites in oxide superconductors are lower by 1 eV. However, the Cu $3d$ and O $2p$ bands are nearly coincident in these materials while they are separated by 3 eV in CuO. Furthermore, in Y-Ba-Cu-O compounds, a strong relation was found between the intensities of the satellite and the main peak suggesting that the degree of the Cu-O hybridization may change the intensity of the satellite.[16] From the results of the previous work in Ni, NiO, and CuO,[22,24,25] we assume that the satellites in oxide superconductors arise from a two-hole bound state at the Cu site. Using the *simple model* with a *single level* described in Sec. II and assuming that this level lies near the main photoemission peak at 5 eV below E_F, we estimate that U_{Cu} needs to be an order of 7 eV to yield the measured binding energy for the satellite.

Utilizing a more realistic band structure[30] for La_2CuO_4 calculated from the density functional theory, we performed the calculations explained in the previous section. It is assumed that the Cu electrons occupy a single band, thus the number of holes is small as required for the validity of the t-matrix approximation. However, the assumption of a one-band model for the Cu states creates an uncertainty in our calculated values of U_{Cu}. Using the Cu densities of states for ρ_0 in Eq. (4), a two-hole Green function at the Cu site can be calculated. To obtain Cu $3d$ hole self-energies, we take the number of unoccupied $3d$ states above E_F to be 0.6 which is estimated from the results of the band theories[28–33] and photoemission data.[7] Figure 2 shows our calculated spectral function for the

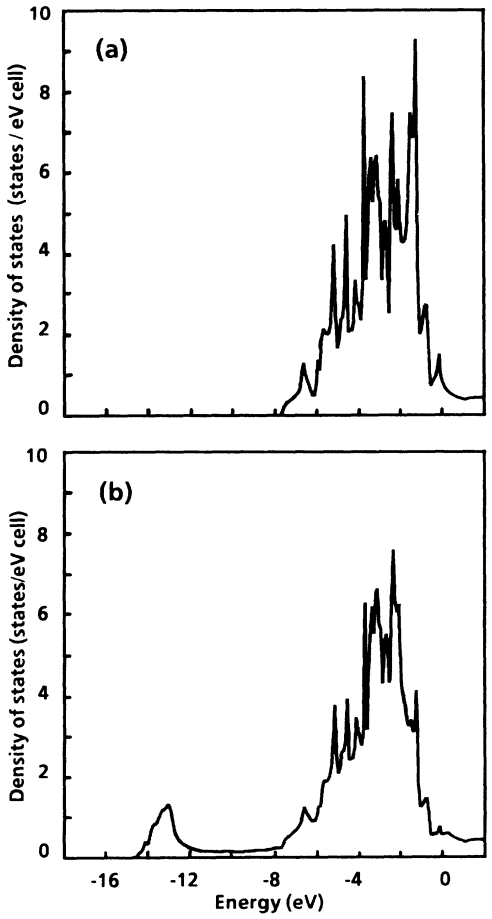

FIG. 2. Spectral densities for La_2CuO_4 of (a) the bare hole states (Ref. 30) and (b) the self-energy–corrected hole states. Energies are measured with respect to the Fermi level.

hole states in La_2CuO_4. The spectral density shows a new peak at about 13 eV below E_F which is assigned to the satellite observed in the photoemission spectra. We also find a peak in the imaginary part of t at the same energy. Since the spectral function includes self-energy corrections only from the Cu sites, the satellite can be viewed as resulting from the strong correlations between $3d$ holes. Our calculated binding energy of 13 eV below E_F for the satellite is in reasonable agreement with the photoemission data when the on-site Cu correlation energy U_{Cu} *is chosen as* 5 *eV*. This value for U_{Cu} is in good agreement with other suggested values from photoemission spectra and cluster model calculations.[7,12,15] In our calculations, we find that U_{Cu} can vary by about 1 eV because the main peak of the one-electron bands used in Eq. (4) lies at 1–2 eV lower energy than in experiments and the Coulomb exchange interaction neglected here is an order of 1 eV. In view of this uncertainty, the present result for U_{Cu} can be considered as a reasonable estimate.

As we discussed before, the intensity of the satellite is roughly proportional to the number of unfilled $3d$ states above E_F. Although the ratio of intensities for the satellite and the main valence band shown in Fig. 2 is in reasonably good agreement with the measured spectra, the agreement is fortuitous because the calculations have limitations in providing both the correct intensity and the position of the satellite. Although the method is semiquantitative, the satellite intensity is expected to be enhanced at resonance because of a super-Koster-Kronig transition as in the case of Ni and CuO.

Recently, there have been several efforts to calculate the Coulomb parameter U from the density functional theory,[42,43] which suggest that the on-site Cu correlation energy ranges from 9 to 12 eV. These calculated energies are somewhat larger than our results and other experimental measurements.[7,12,15] In these calculations, surprisingly large correlations are also found for electrons at O sites with U_O ranging from 6 to 8 eV. In fact, some photoemission experiments[9,14] showed a satellite feature at about 9 eV below E_F which may be associated with correlations on O sites. Using the same t-matrix approach, we find a smaller correlation energy for U_{O} of about 2 eV between O $2p$ holes. Because the binding energy for the O satellite is smaller than the one for Cu, the weaker correlations can be expected.

Since the satellite observed at around 12–13 eV corresponds to the $3d^8$ final state, the excitation of Cu^{3+} will cost a large energy of order U_{Cu}, as pointed out by Shen *et al.*[12] Therefore, holes generated from either Sr doping in La_2CuO_4 or increasing oxidation in $YBa_2Cu_3O_{6.5}$ must be placed on O sites for energetic reasons. This picture is consistent with the results of the photoemission[10,12,13] and Auger spectra[15] which conclude that the $3d^8$ state is insignificant in the ground state and this is used as a starting assumption in much theoretical work[1] on the high-T_c superconducting mechanism. We have recently examined the possible role of the satellite in enhancing T_c. When a hole at the O site polarizes the electronic medium, two $3d$ holes generated by an electron-hole pair excitation accompanied by a ligand-metal hole charge transfer experience the same Coulomb interaction as that associated with a satellite. We note that doped p holes which will be paired at a superconducting transition are screened by different types of *holes*: a hole on each Cu and ligand site or two holes on the same Cu site when a ligand-$3d$ charge transfer occurs. Since this correlation is related to the localized states, the polarization has little dependence on momentum so that an attractive interaction between holes at the O sites extends to large momentum. Details of the calculations will appear elsewhere.[44]

An interesting question is whether the satellite feature is related to the modification of the valence band structures. The valence band width in Ni photoemission was shown to be narrower than the calculated values while for Cu with filled $3d$ bands the calculated and observed widths are found to be similar.[22,35,38] In the case of Ni, it was pointed out that self-energies due to electron correlation effects within the empty $3d$ bands can give correct descriptions of the satellite position and the bandwidth.[35,38] In oxide superconductors, the valence bandwidths are similar in calculations and experiments, but the photoemission spectra of the main valence band are shifted by 2 eV to higher binding energy relative to E_F.

Our calculations show that the spectral density near E_F moves to higher binding energy because of the satel-

lite. This movement of the Cu $3d$ states at about 1 eV below E_F may explain qualitatively why the ultraviolet photoemission spectra exhibit a low density of states in this region of energy and also near E_F. In fact, it was shown that one-electron bands of La_2CuO_4 predicts a significant contribution from the Cu $3d$ states near 1 eV below E_F at the Cu $3p$ threshold while the measured spectra is quite low.[45] However, it is not this movement of the density of states that yields a semiconducting state as seen in oxides. Although electron correlation effects have provided a proper description of the satellite feature and the low density near E_F, the position of the main valence band is still not changed within the same framework. Since recent high-energy photoemission spectra[34] show evidence that the difference between the calculated and the measured binding energies for the main band is caused by the surface contamination of data, further study is needed to decide the accurate positions of main valence bands in the oxides.

IV. SUMMARY

We have shown that the satellites observed at 12–13 eV below the Fermi level in some copper oxide superconductors arise from a two-hole bound state at the Cu site. This picture for the satellite is similar to the case of Ni metal. Strong correlation effects between $3d$ electrons are included in quasiparticle energies through a single-band t-matrix approximation. The single-band approximation creates an uncertainty in our calculated value of U_{Cu}. We have shown that this method describes the satellite features semiquantitatively. The calculated of the binding energies for the satellites lead to estimates of the intracorrelation energy; in oxides, an energy of $U_{Cu}=5$ eV is found at Cu sites. This value is in reasonable agreement with other suggested values based on the photoemission spectra. However, we find a smaller intraatomic interaction parameter on the O site of 2 eV compared to the Cu site, assuming that the O satellite lie at 9 eV below E_F. Because the Cu satellite is viewed as being a high-energy excitation with two holes bound via U_{Cu}, the charge state of Cu^{3+} will not appear in the ground state. Moreover, these results suggest that holes generated by Sr doping in La_2CuO_4 and by increasing oxidation in $YBa_2Cu_3O_{7-\delta}$ are placed on O sites. This suggestion is consistent with the previously proposed ones.

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