Satellites from hybridized Cu-O states in $YBa_2Cu_3O_7$

C. Calandra, F. Manghi, and T. Minerva
Dipartimento di Fisica, Università degli Studi di Modena, Via Campi 213A, I-41100 Modena, Italy
(Received 12 June 1990)

The satellite structure of $YBa_2Cu_3O_7$ compound is calculated starting from an accurate description of the bulk band structure and evaluating the self-energy effects arising from the intra-atomic Coulomb repulsion on the copper and oxygen sites. A continuum of satellites of d^8 character originating from the highly hybridized Cu-O bands is found between 8 and 13 eV binding energy. Comparison with the experimental data allows one to explain the behavior of the Cu satellites in resonant photoemission and provides indications about the intrinsic character of the satellite at 9 eV.

The observation of satellites in the valence-band photoemission of high-T_c superconducting compounds[1] is an important feature of their excitation spectra, being a clear signal of the existence of strong electron-electron correlation. In the parent material CuO, $3d^8$ satellites have been observed 10.5 and 12.6 eV below the Fermi energy E_F,[2,3] the attribution of these structures being based upon their resonant enhancement at photon energies around the Cu $3p$ core excitation threshold. Comparable features have been reported in superconductors, but their assignment is less certain. For the case of $YBa_2Cu_3O_{7-x}$ a well-defined Cu $3d$ satellite, showing the expected resonant behavior at the Cu $3p$ threshold, has been found at about 12.5–13 eV binding energy,[4,5] but the presence and the attribution of additional satellite structures are very controversial issues. Structures at 9–10 eV below E_F, showing a resonant enhancement at Cu $3p$ (Refs. 5–7) or O $2s$ (Refs. 5, 8, and 9) thresholds, has been reported by several groups,[1,10] with an intensity largely determined by surface contamination.[11,12] This picture has been further complicated by the recent observation of a resonant behavior of the Cu $3d^8$ feature at the O $1s$ threshold.[13]

The understanding of the normal state of Y-Ba-Cu-O compounds requires a theory able to predict the spectral features observed in the binding energy range between 13 and 9 eV and to identify their nature: in particular to establish whether they are intrinsic or not, what is the relative weight of the intra-atomic Coulomb repulsion compared with the interatomic one, if they arise from two-hole copper and/or oxygen states or correspond to satellite features originated from strongly hybridized Cu-O bands.

Semiempirical approaches, like the impurity and cluster configuration-interaction models, have been successfully used to derive both the main structures and the satellite peaks in the photoemission spectra of CuO and cuprate superconductors.[14–16] However this has been achieved using a rather simplified model of the band structure, assuming a strong wave-function localization and a considerable number of parameters.

In this paper we adopt a different point of view. Because one-electron band calculations have shown to give a reasonable zeroth-order approximation to the excitation spectrum of $YBa_2Cu_3O_7$,[17,18] we believe that the description of many-body effects should be based on the Block eigenfunctions derived from a full band-structure calculation with no assumption on their localization. Recent work in this direction[19,20] has shown that the inclusion of on-site correlation allows us to reproduce some of the features of the experimental spectra, like the low emission near E_F and the satellite around 13 eV, but does not provide an explanation of the presence of any other significant structure below the main band. Here we show that on-site Coulomb correlation can give rise to more than one satellite in the energy range between 8 and 13 eV below E_F *provided that* the theory is developed taking the hybridized nature of $YBa_2Cu_3O_7$ band structure into full account. To our knowledge this is the first paper where the presence of several satellites is derived starting from the detailed band structure and their intrinsic nature is clearly demonstrated.

A full presentation of the theory is planned to be given elsewhere[21] and here we recall the main formulas which are relevant for the discussion of the results. The key quantity describing the photoemission current is the spectral function of the created hole state:[22]

$$A_{\mathbf{k},n}(\omega)=\frac{1}{\pi}\,\mathrm{Im}\frac{1}{\omega-\varepsilon_{\mathbf{k},n}-\Sigma_{\mathbf{k},n}(\omega)}\ , \tag{1}$$

where $\mathbf{k}$ is the lattice wave vector, n the band index, $\varepsilon_{\mathbf{k},n}$ the single-particle eigenstates, and $\Sigma_{\mathbf{k},n}(\omega)$ is the hole self-energy. We assume the single-particle states to be described by a tight-binding Hamiltonian derived from an accurate parametrization of the band structure.[23] Taking advantage of the large filling of the Cu $3d$ and O $2p$ shells in $YBa_2Cu_3O_7$ (the average electronic occupancies are 9.23 and 5.6 electrons at Cu and O sites, respectively), the hole self-energy can be evaluated in the so-called low-density approximation[24] which for a multiband system leads to the expression[21]

$$\Sigma_{\mathbf{k},n}(\omega)=\sum_{\alpha}|c_{\alpha}(\mathbf{k},n)|^2\Sigma_{\alpha}(\omega)\ , \tag{2}$$

where

$$\Sigma_\alpha(\omega)=\sum_\beta \int_{E_F}^{\infty} n_\beta(\varepsilon) t_{\alpha,\beta}(\varepsilon+\omega)\, d\varepsilon \tag{3}$$

with

$$t_{\alpha,\beta}(\xi)=\frac{U_{\alpha,\beta}}{1+U_{\alpha,\beta}G_{\alpha,\beta}(\xi)} \tag{4}$$

and

$$G_{\alpha,\beta}(\xi)=\int_{-\infty}^{E_F} d\varepsilon_1 \int_{-\infty}^{E_F} d\varepsilon_2 \frac{n_\alpha(\varepsilon_1) n_\beta(\varepsilon_2)}{\varepsilon_1-\varepsilon_2-\xi} \ . \tag{5}$$

In these expressions α,β label the different orbitals belonging to the atoms in the unit cell, $c_\alpha(\mathbf{k},n)$ are the coefficients entering the expansion of eigenstates in terms of atomic orbitals, $n_\alpha(\varepsilon)$ is the α-orbital contribution of the single particle density of states, $t_{\alpha,\beta}$ is the t matrix describing multiple scattering between holes, and $G_{\alpha,\beta}$ is the two-hole bare propagator. $U_{\alpha,\beta}$ is the Coulomb repulsion integral between orbitals α,β belonging to the same site, where α,β refer to different Cu $3d$ or O $2p$ orbitals. We have assumed the same value $U_{\alpha,\beta}=U_{\alpha,\alpha}$ for all the five d (three p) orbitals of copper (oxygen) atom.[25] With this approximation we are left with two parameters only, U_d and U_p, giving the repulsion between two holes on Cu or O sites, respectively. In agreement with previous estimates[19] we assumed $U_d=6$ eV and $U_p=2$ eV.

A few comments are in order.

(i) Expression (2) shows that self-energy depends both on the $\mathbf{k}$ vector and on the band index. This dependence is a result of the extension of the t matrix approach to the hybridized multiband case: previous studies[19,20] assumed the complex band structure of high-T_c superconductors to be a superposition of single bands of specific atomic character, ending up in the definition of different (k independent) self-energies and spectral functions for each atomic site. Neglecting the hybridization between orbitals belonging to different sites is clearly an oversimplification for these systems and in fact it allows us to reproduce the characteristic of the measured spectra only in part (just one satellite).

(ii) Due to the peculiar atomic coordination, the chemical bond in $YBa_2Cu_3O_7$ and in the other high-T_c superconducting compounds is strongly asymmetric making the various orbital densities of states $n_\alpha(\varepsilon)$ very different from one another; the situation is quite different from the one for instance of nickel where, due to the cubic symmetry, all the five d orbital contributions to the density of states are almost identical, allowing us to treat the $3d$ states by a *degenerate* Hubbard Hamiltonian.[26] This fact can give rise to extra poles in expression (5) and therefore to extra satellites.

(iii) The low-density approximation has been applied to Ni (Ref. 22) and other superconductors[19] with a comparable d hole number. The validity of this approximation has been questioned and alternative approaches have been proposed for Ni based either on second-order perturbation theory[27] or on an extension of the t-matrix approach to include hole-electron scattering.[26] Due to the high-U_d value perturbation theory cannot be applied to the present case. Electron-hole interaction is expected to affect somewhat the results without modifying however the main conclusion; in view of the extreme complication associated to the multiband effects we have not tried to include this interaction.

Neglecting matrix elements effects the photoemission spectrum is given by the self-energy corrected density of hole states $N(\omega)$ which is obtained from the spectral function as

$$N(\omega)=\sum_{\mathbf{k},n} A_{\mathbf{k},n}(\omega) \ . \tag{6}$$

Figure 1 shows the spectrum obtained for $YBa_2Cu_3O_7$ compared with the calculated single-particle density of states. The main modifications associated with the inclusion of correlation are (a) a lowering of the density of states at the Fermi energy and a shift of the main peaks by a few tenths of eV; (b) a strong reduction of the peak present in the single-particle density of states at about -3.3 eV and entirely associated to d states of chain Cu atoms: due to their high hole number these states are those mostly affected by correlation; (c) a significant increase of intensity between -4 and -6 eV; (d) the appearance of a continuum of two-hole states below the band-band bottom up to -15 eV. This continuum of states is divided into two main groups of structures, one lying at about -13 eV while the other is accommodated between -11 and -7.5 eV with a maximum at about -9.5 eV. The first group has been found in previous calculations[19,20] and attributed to the $3d^8$ satellite observed

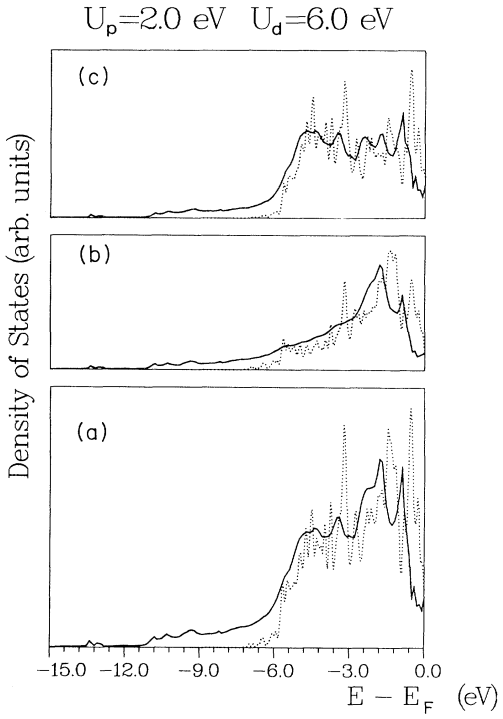

FIG. 1. (a) Spectrum of correlated states obtained with $U_d=6$ and $U_p=2$ eV (continuous line) compared with single particle density of states (dotted line). Panels (b) and (c) show the results of the projection onto copper and oxygen states, respectively.

by resonant photoemission at about this energy. Our results clearly indicate that this is not the only feature of the spectrum and that the on-site Coulomb repulsion may give rise to additional satellites with an even higher intensity at lower binding energies.

As far as the assignment of these satellite structures is concerned we notice that all of them are related to $3d^8$ states and originate from intra-atomic correlation on Cu atoms: this statement is proved by the fact that they are not affected by the neglecting of hole-hole correlation on O sites (see Fig. 2). This does not mean, however, that oxygen states are not involved. Further insight into the nature of the satellite structures may be obtained by projecting the correlated density of states onto the various Cu and O orbitals. Such a procedure allows us to define a correlated *local* density of states:

$$N_\alpha(\omega)=\sum_{\mathbf{k},n}|c_\alpha(\mathbf{k},n)|^2 A_{\mathbf{k},n}(\omega)\ . \tag{7}$$

These partial spectra, shown in Figs. 1(b) and 1(c), provide evidence of the fact that the satellites originate from highly hybridized Cu-O bands, rather than from states that retain the separate identities of the two atoms. An interesting consequence of this fact is that all the satellites should be resonantly enhanced in photoemission at the core-level threshold of both elements. Such a prediction is in agreement with the recent experimental observation of the resonant enhancement of the 13-eV Cu satellite at the oxygen 1*s* threshold, that has been interpreted as a direct evidence of the occurrence of strong hybridization.[13] As to the satellites that we found at lower binding energies, we notice that a clear experimental observation of a resonant behavior at the Cu 3*p* threshold has been reported by Arko *et al.*[5] at 10 eV binding energy proving that d^8 states are present in this energy range. According to these authors this peak is distinct from the feature at 9 eV, whose intensity is strengthened at the O 2*s* threshold, indicating an oxygen derived character. Although a detailed comparison with the experiments is not the purpose of this paper (we have not optimized our U_d and U_p parameters, we have neglected electron-hole interactions and we have not considered surface effects, which are important for a detailed description of the spectra,[28] we believe that our results provide the correct interpretation of this experimental finding.

The presence of two groups of d^8 satellite structures in the range from -8 to -13 eV has been predicted also by the cluster model on the basis of the results for a CuO_6 cluster.[15] However the origin of the structures in our model is different, since they arise from the complex band structure of $YBa_2Cu_3O_7$, in particular from the occurrence of strongly hybridized Cu-O bands, while in the cluster model they are due to the strong Coulomb and exchange splitting of the d^8 multiplet. It is likely that both effects are present in the experimental spectra and that a full account of them may be achieved by a more complete theory, where band and multiplet effects are treated on the same footing.

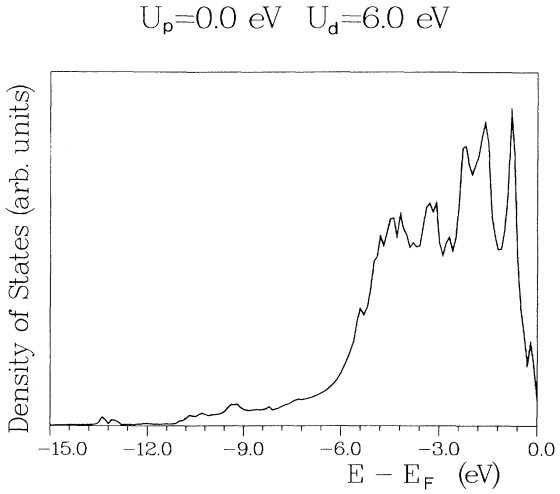

FIG. 2. Spectrum of correlated states resulting by the inclusion of on-site correlation on Cu sites only: $U_p=0$ and $U_d=6$ eV.

Finally, we want to comment about the surface sensitivity of the 9–9.5-eV satellite observed in the experiments, which is taken as an indication of its extrinsic character.[5] We have performed calculations for a finite crystal to account for the surface effects and we have found that for basal plane surfaces the satellites undergo a substantial intensity reduction compared to the bulk.[21] The effect is even more pronounced in presence of an oxygen poor surface phase. Therefore we believe that the structure is intrinsic, but is substantially attenuated at the surface, in agreement with the results for freshly cleaved materials.[17]

In summary we have shown that on-site correlation included via an extension of the low-density approximation to the multiband hybridized case is able to predict the presence of two satellites structures, to assign both of them to Cu d^8 states, and to explain their resonant enhancement at both copper and oxygen thresholds.

One of us (F.M.) would like to thank A. Liebsch for useful discussion and comments on the first draft of this manuscript. Technical and financial support from CICAIA, MURST, and CNR (Progetto Finalizzato Sistemi Informatici e Calcolo Parallelo, Contract No. 89.00011.69) is gratefully acknowledged.

[1]P. A. P. Lindberg, Z.-X. Shen, W. E. Spicer, and I. Lindau. Surf. Sci. Rep. **11**, 1 (1990).

[2]M. R. Thuler, R. L. Benbow, and Z. Hurych, Phys. Rev. B **26**, 669 (1989).

[3]J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Cryzyk, Phys. Rev. B **38**, 11 322 (1988).

[4]J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

[5]A. J. Arko, R. S. List, R. J. Bartlett, S.-W. Cheong, Z. Fisk, J. D. Thompson, C. G. Olson, A.-B. Yang, R. Liu, C. Gu, B. W.

Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, J. C. Campuzano, J. E. Schirber, and N. D. Shinn, Phys. Rev. B **40**, 2268 (1989).

[6]T. Takahashi, F. Maeda, H. Arai, H. Katayama-Yoshida, Y. Okabe, T. Suzuki, S. Hoyosa, A. Fujimore, T. Shidara, T. Koide, T. Miyahara, M. Onoda, S. Shamoto, and M. Sato, Phys. Rev. B **36**, 5686 (1987).

[7]R. L. Kurtz, R. L. Stockbauer, D. Mueller, A. Shih, L. E. Toth, M. Osofsky, and S. Wolf, Phys. Rev. B **35**, 8818 (1987).

[8]Ming Tang, N. G. Stoffel, Qi Biao Chen, D. LaGraffe, P. A. Morris, W. A. Bonner, G. Margaritondo, and M. Onellion, Phys. Rev. B **38**, 897 (1988).

[9]R. L. Kurtz, S. W. Robey, R. L. Stockbauer, D. Mueller, A. Shih, and L. Toth, Phys. Rev. B **39**, 4768 (1989).

[10]J. H. Weaver, H. M Meyer III, T. J. Wagener, D. M. Hill, Y. Gao, D. Peterson, Z. Fisk, and A. J. Arko, Phys. Rev. B **38**, 4668 (1988).

[11]R. S. List, A. J. Arko, Z. Fisk, S.-W. Cheong, S. D. Conradson, J. D. Thompson, C. B. Pierce, D. E. Peterson, R. J. Bartlett, N. D. Shinn, J. E. Schirber, B. V. Veal, A. P. Paulikas, and J. C. Campuzano, Phys. Rev. B **38**, 11 966 (1988).

[12]P. A. P. Lindberg, Z.-X. Shen, J. Hwang, C. K. Shih, I. Lindau, W. E. Spicer, D. B. Mitzi, and A. Kapitulnik, Solid State Commun. **69**, 27 (1989).

[13]D. D. Sarma, P. Sen, C. Carbone, R. Cimino, and W. Gudat, Phys. Rev. B **39**, 12 387 (1989).

[14]G. A. Sawatzky, Int. J. Mod. Phys. B **1**, 779 (1988).

[15]H. Eskes, L. H. Tjeng, and G. A. Sawatzky, Phys. Rev. B **41**, 288 (1990).

[16]A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).

[17]A. J. Arko, R. S. List, Z. Fisk, S.-W. Cheong, J. D. Thompson, J. A. O'Rourke, C. G. Olson, A. B. Yang, Tun-Wen Pi, J. E. Schirber, and N. D. Shinn, J. Magn. Magn. Mat. **75**, L1 (1988); J. C. Campuzano, G. Jennings, M. Faiz, L. Beaulaigue, B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, R. S. List, A. J. Arko, and R. J. Bartlett, Phys. Rev. Lett. **64**, 2308 (1990).

[18]Y. Sakisaka, T. Komeda, T. Maruyama, M. Onchi, H. Kato, Y. Aiura, Y. Yanashima, T. Terashima, Y. Bando, K. Iijima, K. Yamamoto, and K. Hirata, Phys. Rev. B **39**, 9080 (1989).

[19]K. J. Chang, M. L. Cohen, and D. R. Penn, Phys. Rev. B **38**, 8691 (1988).

[20]C. Calandra and T. Minerva, Z. Phys. B **77**, 357 (1989).

[21]C. Calandra, F. Manghi, and T. Minerva (unpublished).

[22]D. R. Penn, Phys. Rev. Lett. **42**, 921 (1979).

[23]M. J. DeWeert, D. A. Papaconstantopoulos, and W. E. Pickett, Phys. Rev. B. **39**, 2269 (1989).

[24]J. Kanamori, Prog. Theor. Phys. **30**, 235 (1963).

[25]L. Kleinman and K. Mednick, Phys. Rev. B **24**, 6880 (1981).

[26]A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1979).

[27]G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B **21**, 3729 (1980).

[28]C. Calandra, F. Manghi, and T. Minerva, Physica C **165**, 461 (1990).