RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 1 1 JULY 1989

X-ray absorption of $YBa_2Cu_3O_7$: A band picture

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(Received 10 March 1989)

Using band-structure theory, we calculate the O 1*s* and Cu 2*p* x-ray-absorption spectra of $YBa_2Cu_3O_7$. The former spectra are in rather good agreement with experiment, showing that the peaks in the low-energy region are due to the van Hove singularity in the chain band. Using core-exciton theory, we argue that this van Hove singularity can survive the strong Cu 2*p*–3*d* Coulomb interaction, giving rise to the "satellite" in the chain Cu 2*p* spectrum.

A central issue in the field of the high-T_c superconductors is the importance of correlation effects. Triggered by the observation of rather strong antiferromagnetism at half filling it is quite fashionable to believe that the high T_c's are characterized by strong electronic correlations, and much speculation has been put forward pointing to a non-Fermi-liquid ground state in these materials and exotic superconductivity. The importance of correlation effects can be studied directly using electron spectroscopy and related techniques. The observation of satellites in the photoemission spectra[1] indicates that correlation effects are playing a role. However, recent observations seem to point to a more conventional bandlike picture. In angle-integrated spectra, Fermi edges and a BCS-like gap[2] have been observed, and dispersions have been found in angular-resolved photoemission spectra.[3] However, it is not yet settled how the total band structure is renormalized and in first instance one would like to know how the highly dispersive Cu 3*d*–O 2*p* σ-type bands[4] are affected. Using the equivalent techniques of core-excitation electron-energy-loss spectroscopy[5] and x-ray absorption (XAS),[6,7] the interesting unoccupied part of these bands has been studied intensively. Especially in the case of $YBa_2Cu_3O_7$, these data contain a wealth of information. However, up to now no convincing interpretation of these data has been put forward and we will show in this Rapid Communication that an appealing picture can be extracted from conventional band-structure theory.

In Figs. 1 and 3 we reproduce the O 1*s* and Cu 2*p* absorption edges for different polarizations as obtained by Nücker *et al.*[5] for $YBa_2Cu_3O_7$. In the former case, the excitation O 1*s* → O 2*p* is studied and the observation of spectral density at low energies is a clear indication of O 2*p* character in the unoccupied density of states (DOS).[5] In the latter case, the 3*d*-unoccupied DOS is sampled (Cu 2*p* → Cu 3*d*), biased by strong core-excitonic effects because of the large Cu 2*p*–Cu 3*d* Coulomb interaction (U_{pd}). For the O 1*s* edge it is well known[8] that excitonic effects are essentially negligible. Finally, it is now well established that the spectra obtained using *c*-polarized light (or electrons) correspond with chain atoms while in *a*-*b* polarization mostly the local DOS in the planes is sampled.[5]

At first sight these data are confusing: What is the origin of the rather narrow peak seen at low energy in the *c*-axis O spectrum? Why is there a similar peak in the *a*-*b* plane O spectrum, although at higher energy than in the former case, while a shoulder appears directly at threshold? What is the origin of the "satellite" in the Cu 2*p* *c*-axis spectrum (Fig. 3), which is absent in the plane direction?[5] It has been argued[6] that this satellite corresponds with a $\underline{p}d^{10}\underline{L}$, and the main line with a $\underline{p}d^{10}$ final state, originating from initial states with $(d^9\underline{L})$, and without (d^9) and additional O 2*p* hole $(\underline{L})$ introduced by doping. However, in this interpretation the absence of a satellite in the *a*-*b* spectrum would imply that there are no holes in the planes, which is highly unlikely.

With respect to the O 1*s* edges, a key observation is that the core hole of the O(4) atom (connecting planes and chains) has a different chemical shift from the plane O [O(2),O(3)] and the connecting chain O [O(1)] core holes (see also Ref. 5). The difference in chemical shifts may by estimated using local-density approximation (LDA) by calculating the different O 1*s* core levels using the self-consistent potential. One finds that the O(4) 1*s* level is shifted by 1 eV towards higher energy, compared to the other O 1*s* levels which are nearly degenerate. Thus, in order to compare the *c*-axis O 1*s* spectrum with the *a*-*b* spectrum, the former should be shifted by 1 eV to higher energy with respect to the latter, assuming that the *c*-axis spectral weight mainly comes from O(4). In this case, the peak in the *c*-axis spectrum is removed from threshold and coincides with the peak in the *a*-*b* spectrum, pointing at a common origin.

In Figs. 1(a) and 1(b) we compare results obtained from LDA calculations using the linear-muffin-tin-orbital method in the atomic-sphere approximation method[9] with experiment. In the lower panel we show the theoretical x,y ($\propto a,b$) [Fig. 1(a)] and z ($\propto c$) [Fig. 1(b)] components of the 2*p* local DOS (LDOS) of the different oxygens.[10] In Fig. 1 we also show the results obtained, taking the optical dipole-matrix elements explicitly into account. As can be seen, the matrix element effects are especially important in the conduction-band region, above ≃4 eV. This is probably due to the strongly antibonding nature of the O 2*p* orbitals in this region.[11] From Fig. 1, it is seen that the valence-band region (below 4 eV) is reproduced quite nicely by the calculations. The LDA *c*-axis result shows a large peak coincident with the peak in the experimental spectrum, and in the *a*-*b* plane the same peak is found and, in addition, a shoulder at threshold. These structures have a simple interpretation: the *c*-axis peak is

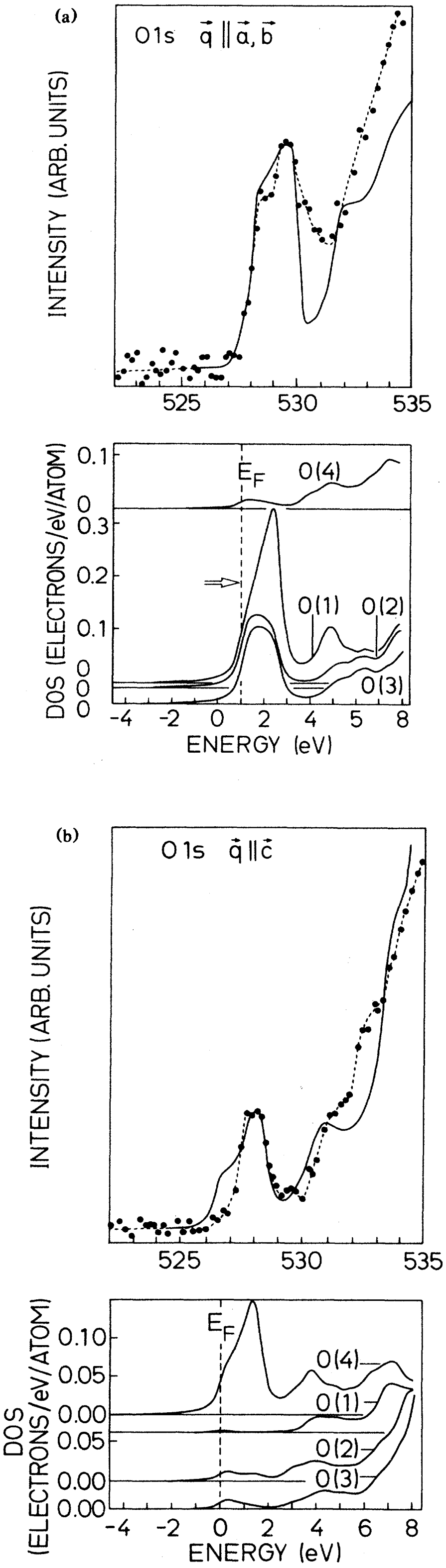

FIG. 1. O 1*s* absorption edges for (a) *a*-*b* and (b) *c* polarized light. Filled circles are the experimental spectra (Ref. 5), solid lines in the upper panels are the full LDA results, and in the lower panels the various 2*p* LDOS of different oxygens is shown.

due to the van Hove singularity at the top of the one-dimensional (1D) chain band, as it shows up in the local $2p_z$ DOS of the O(4) atom. The peak in the *a*-*b* spectrum is also due to this band singularity which is now sampled by the O(1) $2p_y$ orbital. This *a*-*b* peak is superposed on a large background, coming from the two-dimensional bands, sampled by the four oxygen atoms in the planes. Apparently, the only significant discrepancy is that LDA puts too much weight in the chain band near the Fermi energy.

Turning to the Cu 2*p* spectra, it is clear that a simple comparison, as we presented for the O 1*s* edges, does not make sense because of the strong influence of the core hole. However, if the Coulomb interactions between the valence electrons can be effectively neglected, it is well known how to work out the problem.[12] The ground state (Φ_0) can be written as a Slater determinant containing the lowest N_e ground-state orbitals ϕ_k (we only consider one spin direction with N_e electrons per spin direction). The final states (Ψ_f) consist of determinants of size N_e+1, which are constructed using the one-electron orbitals in the presence of the core hole (ψ_l). Neglecting optical dipole-matrix element effects, the spectral density is given by

$$\rho(\varepsilon)=\sum_f |\langle\Psi_f|d_i^\dagger|\Phi_0\rangle|^2\delta(\varepsilon-E_f+E_0)\,, \tag{1}$$

where $d_i^\dagger$ creates a (d) electron at the core-ionized site (i), and E_0 and E_f correspond with the sums of the orbital energies in the ground state and the fth final state, respectively. The total overlaps in Eq. (1) can be rewritten in terms of the Slater determinants of the orbital overlap matrix elements $\langle\phi_k|\psi_l\rangle$ and $\langle\psi_l|d_i^\dagger|0\rangle$ where 0 represents the vacuum state. Because the final-state orbitals are nonorthogonal to the ground-state orbitals for a finite core-hole potential, this leads to a highly nontrivial problem.

Not much is known theoretically[13] about how the total line shape is affected in narrow-band systems. Band filling is, in this respect, an important parameter. It is easy to see that in an empty-band system Eq. (1) reduces to the final-state LDOS. This should also hold approximately in nearly empty band systems, as has been verified for the early 3*d*'s.[14] However, the case under consideration is much closer to the nearly filled band limit. Stated more precisely, a way to picture (believing LDA) the chain z^2-y^2 (or plane x^2-y^2) bands is by first hybridizing the oxygens, resulting in a bonding and a partly filled antibonding band, and then including the Cu-O mixing, transferring some 3*d* weight in the antibonding band,[15] i.e., according to LDA the total *d*-hole count in the chain band ($\langle n_{d(z^2\text{-}y^2)}\rangle$) is quite low ($\simeq 0.4$). In the limit that $\langle n_d\rangle\rightarrow 0$, the XAS spectrum would resemble the initial state *d*-LDOS, as if there is no core hole. This is straightforward to prove from Eq. (1). The physical reason can easily be seen from a configuration interaction consideration; for $\langle n_d\rangle\rightarrow 0$, the ground state can be written as a linear combination of a $|d^{10}\rangle$ state and $|d^9\varepsilon\rangle$ states where ε indicates an electron in the unoccupied part of the band at energy ε. The final states are then $|pd^{10}\varepsilon\rangle$ and the probability to occupy these is equal to their weight in the ground state, i.e., the initial state d-LDOS. Thus, in this limit the 1D band singularity would show up in the Cu(1) spectrum as if there is no core hole.

At the finite hole count, as realized in the high T_c's, things are more complicated. We investigated this problem by studying numerically a three-band model mimicking the chain electronic structure:[16] We took, per unit cell, the Cu(1) z^2-y^2 orbital, two p_z orbitals of the O(4)'s, and the p_y orbital of O(1). In order to get an improved description of the occupied part of the DOS we augmented the model with O(4)-O(1) nearest-neighbor hopping ($t_p = -1.2$ eV) and we used $\Delta = 1.2$, $\alpha = 1$, and $t = -1.2$ (all in eV) as parameters.[16] Using a band filling such that the upper antibonding band is $\frac{2}{3}$ empty, 0.4 out of the $\frac{4}{3}$ holes are found to have $d_{z^2-y^2}$ character, as in the LDA calculation. Finally, in order to represent the core-hole potential, we added the term $U_{pd}n_c n_{di}$ to the Hamiltonian, where n_c and n_{di} represent the number operators for the core hole and d electron at the core-ionized site i. The XAS spectrum can now be easily calculated using the fact that the spectral weight sum rule is rapidly exhausted in a finite system[17] (we used a 90 unit-cell supercell), using an appropriate set of excitations: As a reference set one takes determinants containing the lowest N_e final-state orbitals and one electron in a higher orbital (set 0). With respect to this reference set, excitations are constructed containing one, two, etc., additional electron-hole pairs (set 1, set 2, etc.). In the cases considered by us, $>95\%$ of the total intensity was already contained in sets 0 and 1. In Fig. 2 we show results for the XAS spectra and the final state z^2-y^2 LDOS, using values for U_{pd} spanning the range relevant for experiment [according to core x-ray photoemission spectroscopy (XPS), $U_{pd} \simeq 8$ eV (Ref. 18)]. From the final-state LDOS it can be seen that the d weight above E_F is strongly reduced in the presence of the core hole, and for this model most of the weight goes into a bound state far below the Fermi energy (not indicated in the figure, the bound state at the bottom of the antibonding band has only little d weight). Exciting the deep bound-state electron to unoccupied states gives rise to the core-XPS satellite.[13] In XAS these excitations do not contribute and nearly all the weight is concentrated in the valence-band region. As can be seen, a finite U_{pd} results in a peak at threshold which get sharper for an increasing core-hole potential.[13] However, a clear shoulder is seen at larger energy, coinciding with the band singularity in the LDOS. The weight of this shoulder, relative to that of the threshold peak, is of the same order for 5 eV $< U_{pd} <$ 10 eV as the experimental "satellite" main-line-intensity ratio in the Cu(1) spectrum. In order to check that this shoulder is indeed related to the 1D van Hove singularity, we studied a similar plane model where such a singularity is missing. In this case, no sign of a shoulder is found and instead a single asymmetric line is found, in agreement with the experimental Cu(2) $2p$ spectrum.[5]

Although we have shown that, in principle, the van Hove singularity should show up in the chain Cu spectrum, we do not find a well-developed satellitelike feature in the model results. In this respect it is interesting to consider the LDA Cu(1) LDOS. Because the core-hole potential is a very local perturbation, the LDA Cu d-LDOS in the presence of the core hole can be well approximated by[19]

$$\rho^i(\varepsilon) = \frac{1}{\pi}\,\mathrm{Im}\,\frac{g_0^i(\varepsilon - i0^+)}{1 - U_{pd}\,g_0^i(\varepsilon - i0^+)}\,, \qquad (2)$$

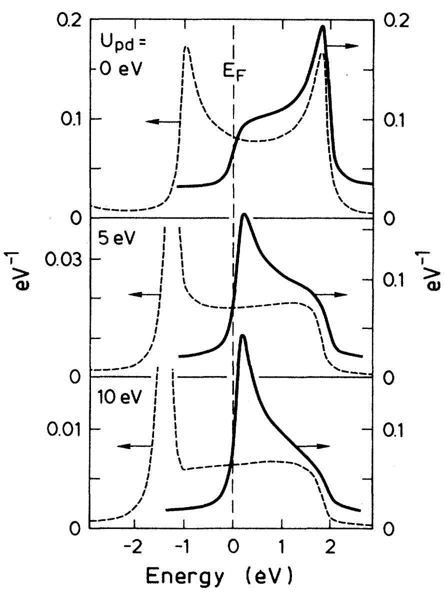

FIG. 2. Results of model calculations for the chain Cu $2p$ absorption spectrum for different core-hole potentials (solid lines). Dashed lines indicate the final state z^2-y^2 LDOS (electron/atom/eV).

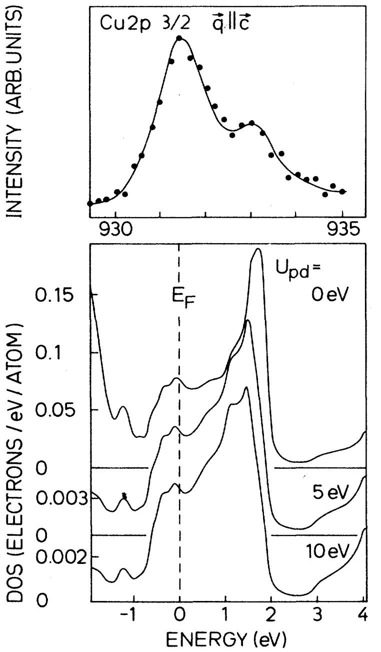

FIG. 3. LDA chain Cu z^2-y^2 LDOS in the absence and presence of an approximate core-hole potential, compared to experiment (filled circles) (Ref. 5).

where g_0^i is the Green's function obtained from the unperturbed LDA-LDOS of a particular local symmetry (i) at one of the Cu sites. At the Cu(1) site, the vast majority of unoccupied d states is of z^2-y^2 character and in Fig. 3 we show the $d_{z^2-y^2}$ LDOS, together with results for a finite core-hole potential, obtained from Eq. (2). The large difference with the model results (Fig. 2) is that according to LDA the 1D band singularity shows up in the LDOS as a peak, even in the presence of a large core-hole potential. This turns out to be a very special property of the LDA-LDOS: We did not succeed in finding a simple model having this feature in common with LDA. Although there is no simple relationship between the final-state LDOS and the spectrum (the initial-state LDOS is probably the first thing to consider), it might well be that this additional final-state LDOS feature can lead to a further sharpening of the van Hove singularity "satellite."

In summary, we have shown that puzzling features in the XAS spectra of $YBa_2Cu_3O_7$ can be explained in a band-structure framework. Can we draw from this some general conclusions concerning the electronic structure of high-T_c materials? First, an attempt similar to ours failed dramatically for the compounds La_2CuO_4 and $YBa_2Cu_3O_6$.[8] In fact, one can deduce from the spectra that in these antiferromagnets a gap is present of about 2 eV, which is absent in the band calculations.[20] From a theoretical viewpoint, interesting physics would be expected if this gap would persist in the doped samples,[21] as in the strong-coupling material NiO.[22] However, if our interpretation is correct this gap has completely vanished in the superconductors and, instead, the band structure looks rather normal, pointing at a Stoner-like picture[23] for the breakdown of the magnetism due to doping. However, even these arguments cannot disprove the existence of a non-Fermi-liquid ground state. Our interpretation of the peaks in the spectra as being due to the van Hove singularity seems to imply that single-particle momentum is quite a good quantum number. On the other hand, recent model calculations[24] seem to indicate that, at least in 1D, spinless fermionlike behavior is found also at a finite U, giving rise to bandlike behavior in the LDOS, while the low-energy quasiparticles (heavily dressed by spin fluctuations) are highly complicated. In this respect, the overestimation of spectral weight at threshold, in the c-axis O 1s spectrum, is quite interesting. This may hint at something more complicated than a simple one-particle band structure in these materials.

We acknowledge helpful discussions with O. K. Andersen, A. Bianconi, J. Fink, O. Gunnarsson, A. M. Oleś, and G. A. Sawatzky.

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