RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 37, NUMBER 7 1 MARCH 1988

Inverse photoemission studies of the high-T_c superconductors

A. J. Viescas, J. M. Tranquada, A. R. Moodenbaugh, and P. D. Johnson
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

(Received 2 October 1987)

We present inverse photoemission spectra recorded from the high-T_c superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$ and the related compound CuO. We are able to identify the various unoccupied orbitals associated with the La, Y, and Ba sites. For the $YBa_2Cu_3O_7$ compound we observe the unoccupied O 2p holes above the Fermi level but do not observe the equivalent holes in the La compound. The inverse photoemission spectrum from CuO shows no pronounced structure.

The observation of higher superconducting transition temperatures in the oxides $La_{2-x}Sr_xCuO_4$ (Ref. 1) ($T_c = 30$ K) and $YBa_2Cu_3O_7$ (Ref. 2) ($T_c \approx 93$ K) has stimulated an enormous research effort into understanding their various properties.[3] Speculation has arisen as to whether the traditional electron-phonon coupling[4] is present or whether some new pairing mechanism is responsible for the superconducting properties. Indeed, several theories have appeared in the literature based on electron-electron or hole-hole interactions.[5,6]

Early attempts[4] to predict the transition temperatures resulting from electron-phonon coupling were reliant on the results of the electronic band structure calculations.[7] However, subsequent photoemission studies attempting to verify these calculations found a discrepancy between theory and experiment as to the absolute binding energies of the different valence features.[8-10] It was suggested that this discrepancy was partly due to the fact that the photoemission spectrum reflects the presence of the photohole and partly due to the fact that the calculations were based on the local-density approximation (LDA).[8-11] In fact, the magnitude of the discrepancy arising from these two different sources is dependent in both cases on the localization or width of the band involved. The further observation of strong satellite structure in the photoemission spectra[12] confirmed that a band description might not be the appropriate means of understanding their electronic properties. Inverse photoemission studies of these materials are therefore imperative. They provide information on the unoccupied densities of states above the Fermi level and allow exploration of the excited-state properties, in that, rather than removing an electron from the system (photoemission), an electron is added producing a negative ion.

In this paper we describe our own detailed inverse photoemission studies of the high-T_c superconducting materials $La_{2-x}Sr_xCuO_4$ with $x = 0.15$ and $YBa_2Cu_3O_7$. It has been suggested that the principal valency of the copper atoms in these materials is Cu^{2+},[13] and we therefore compare our inverse photoemission spectra with that recorded from the oxide CuO in which copper also has the valency 2+.

The experiments were carried out on an apparatus that has been described in detail elsewhere.[14] Briefly, the photons emitted in the inverse photoemission process are detected with a grating spectrograph operating in the range 10–30 eV. For lower incident electron beam energies the overall resolution is determined by the energy spread of the electron source, typically 0.3 eV. At higher energies, e.g., ~30 eV, the resolution is dominated by the wavelength resolution of the spectrograph and is of the order of 0.75 eV.

The $YBa_2Cu_3O_7$ sample was prepared from dried Y_2O_3, $BaCO_3$ reagent and fully oxidized CuO following a variation of the recipe of Cava and co-workers. The lanthanum samples were prepared following a similar method, which has also been outlined previously. The CuO sample was pelletized and then sintered in air for 16 h at 950 °C. Clean surfaces were produced by filing the surface under ultra-high-vacuum conditions.

In Fig. 1 we show the inverse photoemission spectra recorded from $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_7$, and CuO.

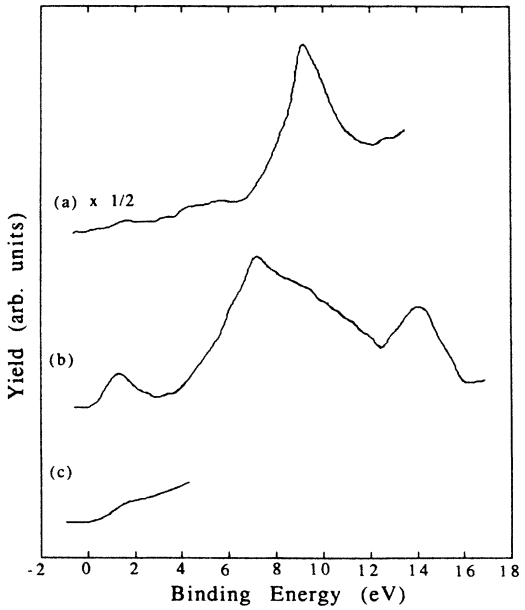

FIG. 1. Inverse photoemission spectra recorded from (a) $La_{1.85}Sr_{0.15}$ CuO_4, (b) $YBa_2Cu_3O_7$, and (c) CuO. The first spectrum is multiplied by the scaling factor indicated. The incident electron beam energies with respect to E_F were (a) 27 eV, (b) 29 eV, and (c) 16.0 eV.

Although not shown here, the spectrum obtained from the undoped La_2CuO_4 was identical to that from $La_{1.85}Sr_{0.15}CuO_4$. The spectrum characteristic of the latter superconductor [Fig. 1(a)] is dominated by a single peak at 9.0 eV and a very low density of states at the Fermi level. Following others we associate the peak with transitions into the unoccupied La 4*f* levels.[15,16] The assymetry in this peak may be indicative of a subsidiary peak closer to the Fermi level as observed in Ref. 15. However, we note that we were never able to clearly resolve a peak. The spectrum recorded from $YBa_2Cu_3O_7$ shown in Fig. 1(b) is similar to that published previously by Yarmoff *et al.*[17] in that a peak is observed immediately above the Fermi level, with another peak at 7.0 eV above the Fermi level. The latter peak at 7.0 eV we associate with the Ba 5*d* and Y 4*d* bands. We observe a further peak at 14.0 eV, which we associate with the unoccupied Ba 4*f* levels.

The peak immediately above the Fermi level in Fig. 1(b) has an intensity dependent on the state of cleanliness of the surface. Thus it is most intense immediately after scraping and slowly disappears as a function of time. With such behavior and based on our earlier photoemission experience[8] we associate this peak with unoccupied oxygen 2*p* states but note that there is probably also a copper 3*d* component as suggested in band-structure calculations.[11,18] This picture gains support if we compare the spectrum in Fig. 1(b) with our measurement of the unoccupied states immediately above the Fermi level in CuO [Fig. 1(c)]. As stated earlier, CuO nominally has a copper valency of 2+, with one Cu *d* hole but no empty oxygen 2*p* states. It will be seen in Fig. 1(c) that only a very weak structure at approximately 1.5 eV is observed above the Fermi level.

Recent photoemission studies have shown that the $YBa_2Cu_3O_7$ surface tends to react with water producing a hydroxide surface.[19] Indeed the peak immediately above the Fermi level could be evidence of hydroxide species. However, we note that the photoemission studies did not indicate a reduction in the characteristic hydroxide features as a function of time but did show a reduction in the oxygen component.

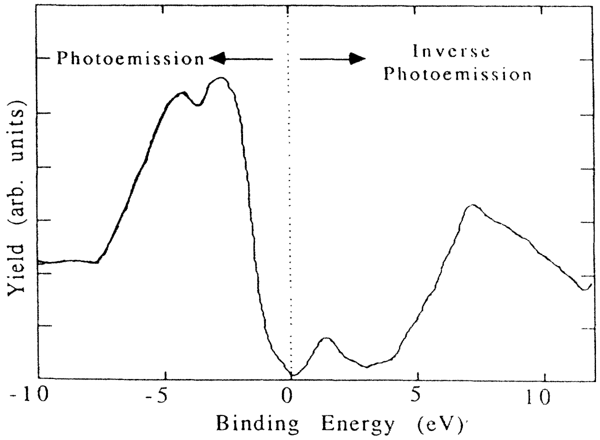

FIG. 2. A comparison of the photoemission and inverse photoemission spectra recorded from the superconductor $YBa_2Cu_3O_7$. The procedure for scaling these spectra is given in the text.

When the electron added in the inverse photoemission process ends up in an atomiclike final state, its final energy will depend on the amount of screening charge present. In Fig. 1(a) the La 4*f* levels appear at approximately 9.0 eV above the Fermi level as opposed to 5.5 eV observed in pure La metal, indicating that the superconductor is relatively ionic. In Fig. 1(b) the Ba 5*d* and Y 4*d* levels are observed 7 eV above the Fermi level. Mattheiss and Hammann,[18] calculating the band structure of $YBa_2Cu_3O_7$, place these levels at 4.75 eV above the Fermi level. The difference between theory and experiment again reflects in part the difference between an excitation spectrum and a ground-state calculation. We note that in the photoemission spectra from this material the difference between theory and experiment in the binding energies of the occupied Ba core levels is approximately 5.0 eV. We anticipate that these latter Ba core levels will be more localized than the unoccupied *d* bands above the Fermi level.

It is of interest to compare the relative density of states above the Fermi level for the $YBa_2Cu_3O_7$ compound with the extremely low density of states previously observed below the Fermi level in our photoemission studies.[8] A direct comparison is not easy because of the many different normalizations required for the two different experiments. In order to make an approximate comparison we firstly assume that the measured occupied valence band consists entirely of Cu 3*d* and oxygen 2*p* electrons. At 40.8 eV the oxygen 2*p* and copper 3*d* photoionization cross sections are almost equal. We then make the assumption that the unoccupied Ba 5*d* and Y 4*d* states have a similar cross section in the inverse photoemission studies and therefore use calculated cross sections for the Y 4*d* level. At 27 eV incident energy the Y 4*d* and O 2*p* level will have a similar cross section. We therefore normalize the two sets of data, the 40.8-eV photoemission spectrum and the 27-eV incident energy inverse photoemission spectrum, such that the observed densities of states scale according to 58 valence electrons below the Fermi level and a total of 29 Ba 5*d* and Y 4*d* hole states above the Fermi level. The results of this procedure are shown in Fig. 2 where we compare the earlier photoemission spectrum with the unoccupied states observed in the present study. We note that the combined width of the valence bands from our photoemission and inverse photoemission studies is 9.5 eV as compared to 7.5 eV found in the calculated density of states.[18] Naively integrating the unoccupied density of states immediately above the Fermi level in Fig. 2 produces a hole count of between 2 and 3. This number is higher than one would expect from valency arguments for the oxygen hole count and may reflect cross-sectional effects not correctly accounted for in our approximation.

Comparing the inverse photoemission spectrum in Fig. 2 with the band-structure calculation of Mattheiss and Hamann shows reasonable agreement between the experimentally observed binding energy of the oxygen derived feature and the density of states associated with the top of the calculated oxygen bands. This agreement is surprising in view of the disagreement found in all earlier photoemission studies of the occupied levels. As noted earlier it has been suggested that the latter disagreement is partly due to errors in the LDA calculation and partly a reflection of the fact that photoemission represents an excited state. The self-interaction error in the LDA calculation will be less the closer the level is to the Fermi level. Further, one anticipates that the excited state associated with inverse photoemission will result in the observed levels being pushed towards the vacuum level away from the Fermi level as is indeed observed for the Ba 5*d* levels. Thus, it may be fortuitous that better agreement is observed between the present experiment and the band-structure calculation.

Various coupling mechanisms have been proposed to describe the superconducting properties based on the presence of oxygen or copper holes within the two-dimensional CuO_2 planes. Our experiments on $YBa_2Cu_3O_7$ indicate the presence of oxygen holes above the Fermi level but we are unable to clearly identify any copper *d* component. Shown in Fig. 1 we note however that we are not able to positively identify the copper *d* hole in CuO either. The question arises as to why we do not observe a peak immediately above the Fermi level in the $La_{1.85}Sr_{0.15}CuO_4$ superconductor. One possible explanation is that it has been observed in Hall effect experiments[20] that T_c scales with the number of carriers. If the oxygen holes are the carriers, as has been suggested in the theory of Emery,[6] we would expect the oxygen peak in the inverse photoemission spectrum for the La compound to be approximately one-third that for the Ba compound. Such a small peak may prove to be unobservable within the experimental resolution and low signal of the present study. We note however that electron-energy-loss-spectroscopy and x-ray-absorption[13] studies elsewhere indicate the possible presence of oxygen hole states in this material with increased doping.

Finally, we make the observation that our studies indicate no fluorescence following the radiative decay of low-lying core holes in either Ba, Y, or La. Elsewhere we have clearly identified fluorescence from clean niobium following ionization of the low-lying 4*p* core level.[21] This would suggest that the Y and La *d* electrons have indeed been pushed out of the occupied valence bands as indicated in calculations.

In summary, our studies show the presence of oxygen hole states above the Fermi level in the $YBa_2Cu_3O_7$ compound but do not reveal a similar peak in the $La_{1.85}Sr_{0.15}CuO_4$ compound. Our studies do not appear to be sensitive to the presence of copper *d* holes as witnessed by the lack of observation of such in CuO. Our results for $YBa_2Cu_3O_7$ may be interpreted as showing agreement with earlier band-structure calculations. However, we note again that such agreement is surprising in view of the strong correlation effects observed elsewhere in both the present spectra and earlier photoemission studies.

The authors would like to acknowledge useful discussions with V. J. Emery. This work was supported by Materials Sciences Division, Department of Energy under Contract No. DE-AC02-76CH00016.

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, A. J. Juang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] V. J. Emery, Nature **328**, 756 (1987).

[4] W. Weber, Phys. Rev. Lett. **58**, 1371 (1987).

[5] P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[6] V.J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).

[7] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1024 (1987).

[8] P. D. Johnson, S. L. Qiu, L. Jiang, M. W. Ruckman, Myron Strongin, S. L. Hulbert, R. F. Garrett, B. Sinkovic, N. W. Smith, R. J. Cava, C. S. Jee, N. Nichols, E. Kaczanowicz, R. E. Saloman, and J. E. Crow, Phys. Rev. B **35**, 8811 (1987).

[9] A. Fujimori, M. Saeki, N. Kimizuka, M. Tanigukchi, and S. Suga, Phys. Rev. B **35**, 8814 (1987).

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

[11] J. Redinger, A. J. Freeman, J. Yu, and S. Massidda (unpublished).

[12] P. Thiry, G. Rossi, Y. Petroff, A. Reucoleoschi, and J. Jegndez (unpublished).

[13] J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh, and M. Suenaga, Phys. Rev. B **35**, 7187 (1987).

[14] P. D. Johnson, S. L. Hulbert, R. F. Garrett, and M. R. Howells, Rev. Sci. Instrum. **57**, 1324 (1986).

[15] T. Riesterer, J. G. Bednorz, K. A. Mueller, and B. Reihl, Appl. Phys. A **44**, 81 (1987).

[16] N. Nucker, J. Fink, B. Renker, D. Ewert, C. Politis, J. W. P. Weijs, and J. C. Fuggle, Z. Phys. B **67**, 9 (1987).

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

[18] L. F. Mattheiss and D. Hamann, Solid State Commun. **63**, 395 (1987).

[19] S. L. Qiu, M. W. Ruckman, N. Brookes, P. D. Johnson, J. Chen, C. L. Lin, M. Strongin, B. Sinkovic, J. E. Crow, and Cham-Soo Jee, this issue, Phys. Rev. B **37**, 3747 (1988).

[20] N. P. Ong, Z. Z. Wang, J. Clayhold, J. M. Tarascon, L. H. Greene, and W. R. Mckinnon, Phys. Rev. B **35**, 8807 (1987).

[21] X. Pan and P. D. Johnson (unpublished).