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Empty states near the Fermi level in $Bi_2Sr_2CaCu_2O_8$

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Unoccupied states are seen at the Fermi level in $Bi_2Sr_2CaCu_2O_8$ by use of inverse photoemission. They have partial oxygen $2p$ character, as evidenced by a resonance at the O $2s$ core-level threshold and by the similarity between the inverse photoemission spectrum and the O $1s$ absorption edge. These states are likely to be related to the hole states introduced by doping of oxide superconductors. A peak at $E_F+2.9$ eV can be assigned to the unoccupied Cu $3d$ states (if they are localized) or to the Bi $6p$ states (for delocalized Cu $3d$ states).

The mechanism for superconductivity in the oxide superconductors is still unclear. We know that holes (and not electrons) are responsible for superconductivity from the correlation that has been established between the transition temperature T_c and the hole concentration, as measured by wet chemistry and the Hall effect.[1] Therefore, the study of unoccupied states just above the Fermi level E_F is of prime interest to understanding the superconducting hole states. An open question is the character of these states, which could be bandlike (Fermi liquid) or localized (Hubbard model, resonant valence bond). Empty states have been studied with soft x-ray absorption[2-5] and electron-energy-loss spectroscopy,[6-8] and their atomic character has been revealed. At the Cu $2p$ absorption edge, the transitions into the empty Cu $3d$ states corresponding to the $3d^9$ configuration of Cu^{2+} have been observed. Upon doping, additional holes are created, which appear at the O $1s$ edge, not at the Cu $2p$ edge. From these measurements it is clear that there exist unoccupied Cu $3d$ and O $2p$ states within a few eV of the Fermi level. However, their exact energy location cannot be determined since the Coulomb interaction of the electron with the core hole shifts the optical transition towards lower energy. This excitonic shift can amount to several eV.

In order to exactly locate the energy position of the unoccupied states we have performed inverse photoemission experiments on $Bi_2Sr_2CaCu_2O_8$. We find unoccupied states that extend all the way down to the Fermi level. In previous inverse photoemission experiments from high-temperature superconductors[2,6,9-13] the density of states decreased strongly when approaching the Fermi level, and it was not clear whether or not there was a Fermi liquid. By varying the energy of the incident electrons we observe that the states at the Fermi level exhibit a resonance when reaching the O $2s$ core-level threshold, analogous to a resonance observed for the occupied states[14] at the Fermi level. These findings suggest the existence of a metallic band of partial O $2p$ character extending continuously through the Fermi level. Put differently, the superconducting holes have delocalized (bandlike) character, although the pairing mechanism might well involve localized Cu $3d$ states.

The choice of $Bi_2Sr_2CaCu_2O_8$ is motivated by the ease of surface preparation. Single crystals cleave well, like a layered compound, and exhibit much less tendency to be contaminated than the other high-temperature superconductors. In photoemission experiments it is easy to obtain emission at the Fermi level, whereas for the other materials such metallic behavior has been observed only in a few cases. We expect a similar situation in inverse photoemission.

Single crystals of $Bi_2Sr_2CaCu_2O_{8+x}$ ($x\approx 0.15$) were grown from polycrystalline material of composition $Bi_4Sr_3Ca_3Cu_4O_y$ maintained at about 875 °C for 40–50 h in air. The crystals were obtained as thin plates, which were up to about $3\times3\times0.5$ mm^3 in size with the c axis perpendicular to the plates. Typically, the onset of the superconducting transition was about 84–85 K. An analysis indicated that the composition was near to $Bi_{2.1}Sr_{1.6}CaCu_2O_{8.15}$ with excess oxygen beyond the stoichiometric compound. Single-crystal x-ray examination confirmed the incommensurately modulated $\sqrt{2}\times\sqrt{2}$ orthorhombic cell. Various methods for preparing clean surfaces were tried. Scraping produced clean surfaces, although the roughness increased upon prolonged scraping, and all spectral features broadened. The best results were obtained by cleaving in vacuum (mid-10^{-10} Torr range) using a tab technique. Occasionally the cleave occurred along a plane containing intercalated impurities. Such cleaves could be detected easily by the electron-stimulated desorption of the surface contaminant during the inverse photoemission experiment. They exhibited less emission near the Fermi level. The experiments were performed with a spectrograph[15] that allowed tuning of the photon energy for studying resonance effects. An overall energy resolution of 0.3 eV could be achieved, which is the state of the art in inverse photoemission. For an accurate energy calibration we used spectra taken from a gold crystal before and after the superconductor measurements.

An overview spectrum of $Bi_2Sr_2CaCu_2O_8$ is given on the bottom of Fig. 1. Its main features are a metallic Fermi edge and a relatively sharp peak at $E_F+2.9$ eV. The intensity and width of the latter varies somewhat with sample preparation as indicated by the dotted curve. The height of the Fermi edge is reproducible as long as the sample surface is clean. Compared to a Au reference sample it is about 5 times (2 times) smaller at initial energies E_i of 12 eV (18 eV) above E_F. A closeup view of the Fermi edge with better resolution (Fig. 2) shows that there are states all the way down to the Fermi level, at

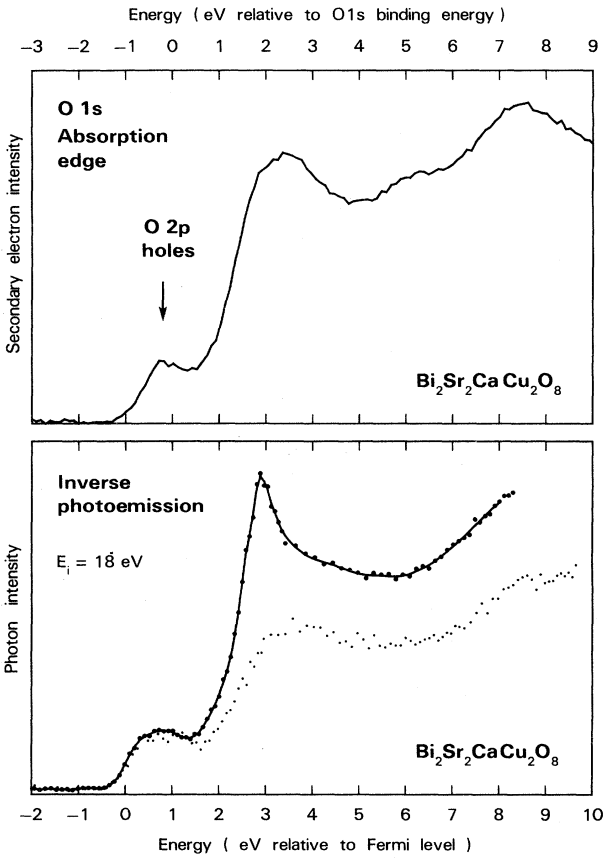

FIG. 1. Unoccupied states of $Bi_2Sr_2CaCu_2O_8$ measured by inverse photoemission (bottom) and by soft x-ray absorption (top, from Ref. 5). The two inverse photoemission spectra span a range of different sample preparation.

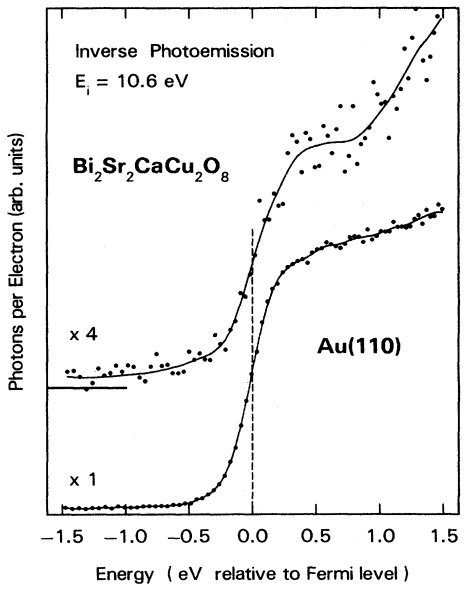

FIG. 2. Closeup view of unoccupied states near the Fermi level in $Bi_2Sr_2CaCu_2O_8$, exhibiting metallic states near the Fermi level. The spectrum from a Au(110) surface is given for comparison.

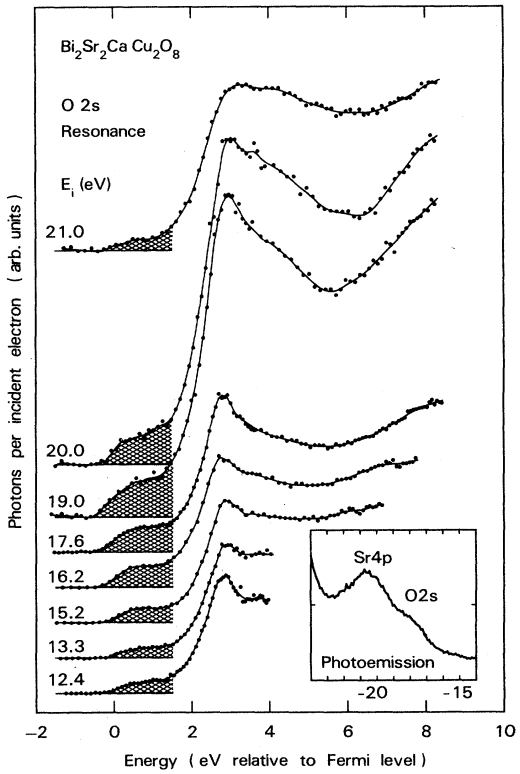

FIG. 3. Resonance of the inverse-photoemission intensity at an initial energy $E_i \approx E_F + 19.5$ eV, i.e., just above the O 2s core-level threshold (see inset). The resonant behavior of the unoccupied states at E_F is similar to that of the occupied states near E_F (compare Ref. 14) and suggests a continuous band of O 2p character crossing the Fermi level.

least within a fraction of our energy resolution of 0.3 eV. [The latter is determined as the full width at half maximum (FWHM) of the derivative of the Au spectrum in Fig. 2.] The density of states decreases at 1.5 eV above E_F in our best samples before the large peak at 2.9 eV sets in. This decrease probably delineates the upper edge of the metallic band around the Fermi level.

The character of the states at the Fermi level is at least partially O 2p-like. This can be concluded from two observations. First, the inverse photoemission spectrum is rather similar to the O 1s absorption (Fig. 1), which represents the density of p-like states projected onto the oxygen atom. This is not too surprising since the inverse photoemission cross section of the O 2p states dominates over that of the Cu 3d states for the energy regime considered here.[16] The main difference between the two spectra in Fig. 1 is that the absorption spectrum is shifted down by 1 eV relative to the inverse-photoemission spectrum. This shift can be explained by electron-hole Coulomb interaction, although the exact magnitude of this interaction is rather uncertain since the energy calibration in the absorption experiment[5] is only accurate to ± 1 eV. A second piece of evidence in favor of oxygenlike character of the metallic band is a resonance phenomenon[17] at the O 2s core-level threshold (Fig. 3). When the initial ener-

gy E_i of the incoming electron approaches $E_F+19.5$ eV, the intensity of the Fermi edge increases by more than a factor of 2. The binding energy of the shallow O $2s$ core level is about 18 eV below E_F (inset in Fig. 3), i.e., close to the resonance energy. An analogous resonance has been observed[14] for the occupied states just below the Fermi level. By combining inverse photoemission with photoemission one arrives at a band of oxygen $2p$ character extending from about 1 eV below E_F to 2 eV above E_F.

The structure at $E_F+2.9$ eV appears to be more complex than the emission at the Fermi edge. It seems to be composed of a sharp feature superimposed on a broader steplike background. (Compare the two inverse photoemission spectra in Fig. 1, which show that the intensity of the 2.9-eV feature, depends somewhat on the preparation conditions.) The broad step has oxygen character since it is present in the O $1s$ absorption spectrum (Fig. 1), and is resonantly enhanced at an initial energy $E_i=E_F+19.5$ eV (Fig. 3), i.e., the same as for the Fermi-level emission.[17] This feature can be assigned to the antibonding counterpart of the occupied O $2p$ valence band. The sharp feature does not resonate at the O $2s$ core-level threshold, and it is absent in the O $1s$ absorption edge. Its assignment depends on whether or not the Cu $3d$ states are localized in the high-temperature superconductors. In a delocalized band picture[16,18] the Cu $3d$ states are expected to be hybridized with the metallic O $2p$ band near the Fermi level. In this case the extra peak at 2.9 eV can be assigned to the Bi $6p$ states. The higher-lying Sr $4d$ and Ca $3d$ states are less likely candidates. If the Cu $3d$ states are localized, they split into two bands separated by the Cu d-d Coulomb interaction. The upper band corresponds to the Cu $3d^{10}$ configuration, which is obtained when adding an electron to the Cu $3d^9$ ground state in the inverse-photoemission experiment, the lower band corresponds to the Cu $3d^8$ configuration, obtained by removing an electron in photoemission. In this case the sharp feature at $E_F+2.9$ eV can be assigned to the upper Cu $3d$ band. In Hubbard-like models[19,20] for localized Cu $3d$ electrons, the upper band is placed near this energy, separated by the Cu d-d Coulomb interaction [about 5.6 eV (Ref. 5)] from the lower band [about 3.5 eV below E_F (Ref. 5)].

Note added in proof. We have become aware of two recent inverse photoemission studies of $Bi_2Sr_2CaCu_2O_8$ which report results similar to ours: T. J. Wagener, Y. Hu, Y. Gao, M. B. Jost, J. H. Weaver, M. D. Spencer, and K. C. Goretta, Phys. Rev. B **39**, 2928 (1989) and R. Claessen, R. Manzke, H. Carstensen, B. Burandt, T. Buslaps, M. Skibowski, and J. Fink (unpublished).

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