Origin of the electronic states near the Fermi level in high-T_c superconductors

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We have studied superconducting and insulating Cu-oxide systems by photoemission spectroscopy. The emission feature near the Fermi level E_F for $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ remains unchanged when hole carriers are depleted by Y substitution for Ca. A similar feature is observed also for insulating $Sr_2CuO_2Cl_2$. These facts suggest that the feature near E_F in the Bi compounds is due to states which are split off out of the oxygen p band, possibly through hybridization with Cu d^8 states, and cannot be due to a Kondo-type resonance and resulting renormalized heavy-electron band states. Other origins for the states near E_F in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ are also discussed.

Although it is obvious that the conductivity in Cu-oxide superconductors is realized by doping antiferromagnetic insulators with extra carriers, the nature of the resulting normal metallic states has been the subject of fundamental controversy. Originating from Anderson's resonating-valence-bond picture, the properties of a small number of holes introduced into Mott insulators have been extensively studied in the framework of strong-coupling theories.[1] Now that it has been established that the band gaps in the undoped Cu oxides are not of the original Mott-Hubbard-type but of charge-transfer-type and that extra holes go into oxygen p orbitals,[2] recent research is focused on the behavior of p-hole carriers interacting with nearly localized Cu d electrons.[3] An opposite viewpoint to describe the electronic states in high-T_c superconductors is to start with normal Fermi-liquid states consisting of oxygen p and copper d energy bands for the doped compounds.[4] In this Fermi-liquid approach, in analogy with f-electron systems, one considers a Kondo-type many-body resonance of Cu d character and resulting renormalized heavy-electron bands formed in the vicinity of the Fermi level, E_F.

In the light of the above two extreme theoretical points of view, further experimental information on the electronic structure of the high-T_c superconductors is clearly needed. The density of states (DOS) within $\lesssim 1$ eV of E_F of the oxide superconductors as observed by photoemission spectroscopy is generally quite low as compared to those of usual metals, but is still finite with discernible Fermi edges.[5-9] In recent angle-resolved photoemission studies on Bi-Sr-Ca-Cu-O superconductors,[10] dispersive states crossing E_F have been identified in this low DOS region: This observation has provided evidence for Fermi-liquid states and further has been taken as an indication of renormalized-band formation near E_F.[10] Another interpretation of the dispersive Fermi-liquid states near E_F may be that they originate from states which are split off from the oxygen p band into the O p–Cu d (d^{10}) charge-transfer gap. Such split-off states may be formed as a result of hybridization between the oxygen p band and the Cu d (d^8) states as described by the impurity Anderson model[11] or the cluster model.[12] The Cu d^9–O p hole local singlets ($^1A_1$ states), which constitute a basis for the recent effective-Hamiltonian approaches to the original Cu d–O p two-band model,[13] are a likely candidate for the hybridization-induced split-off states. The split-off states can preexist in the insulators: Hole doping locates E_F within these states leading to the formation of Fermi-liquid states. (We note, however, that the introduction of excess oxygens or the alkaline-earth atom substitution for rare-earth atoms aiming at hole doping itself may also produce split-off states through hybridization[14] or electrostatic interaction,[15] respectively. We will return to this point below.) Figure 1 summarizes the above models for the doped and undoped Cu-oxide systems.

Thus the doping dependence of photoemission spectra near E_F is expected to provide valuable information on the origin of these states. In this paper, we present the results of our photoemission study on metallic and insulating Cu-oxide materials, with particular emphasis on the electronic states near E_F. Our results on insulating samples indeed show essentially the same feature as those observed for metallic samples and give support to the split-off oxygen p states rather than the Kondo-type resonances as the origin of the Fermi-liquid states.

Photoemission spectra were taken using He I and He II ($h\nu = 21.2$ and 40.8 eV) resonance lines with a resolution of ~ 0.15 eV. Satellites of the radiation sources have been numerically subtracted. For these photon energies, the O $2p$ photoionization cross section dominates the Cu $3d$ cross section.[16] We have measured spectra on single crystals of $Bi_2Sr_2CuO_6$ (one CuO_2 layer, $T_c \lesssim 10$ K) and $Sr_2CuO_2Cl_2$ (insulator) grown by the flux method and a sintered pellet of $Bi_4Sr_3(Ca_{0.58}Y_{0.42})_3Cu_4O_{16+\delta}$ (two

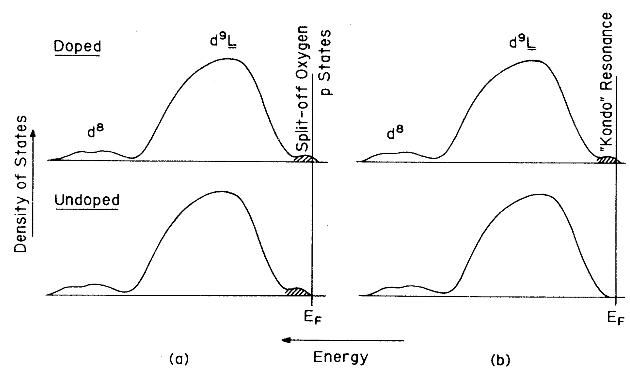

FIG. 1. Schematic representation of oxygen p-derived density of states for doped and undoped Cu oxide materials. (a) Split-off oxygen states which preexist in the insulators as a result of, e.g., hybridization with the Cu d^8 states. (b) Kondo-type resonance and associated renormalized-band states formed when the system is doped with extra holes. Note, however, that split-off oxygen states created by the doping process itself (see text) may show a behavior similar to (b) rather than (a).

CuO_2 layer, insulator).[12] The spectra of $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ (two CuO_2 layer, $T_c \simeq 80$ K) have been taken from Ref. 8. In the $Bi_4Sr_3(Ca_{0.58}Y_{0.42})_3Cu_4O_{16+\delta}$ sample, hole carriers have been depleted by Y substitution for Ca: The absence of metallic carriers was confirmed by Meissner volume fraction[17] and thermopower measurements. In order to obtain clean surfaces, the samples were scraped *in situ* with a diamond file in a vacuum in the 10^{10}-Torr range. A single-peaked O 1s core-level x-ray photoemission spectrum and the absence or weakness of emission at ~9 eV below E_F for every sample demonstrated that the surface was indeed clean and free from degradation.[18]

Figure 2 shows photoemission spectra of the metallic and insulating Bi compounds. Both the one- and two-CuO_2-layer superconductors show weak emission within ~1 eV of E_F with finite DOS at E_F indicating metallic character of these compounds, although the former compound shows a lower DOS at E_F in agreement with the result of Shen *et al.*[7] and a wider weak emission region than the latter (~1 vs ~0.8 eV). The spectrum of the two-CuO_2-layer insulator $Bi_4Sr_3(Ca_{0.58}Y_{0.42})_3Cu_4O_{16+\delta}$ is virtually identical to that of the two-CuO_2-layer superconductor except for the shift of the whole spectrum to higher binding energy by ~0.2 eV and the concomitant suppression of the DOS at E_F. This behavior clearly indicates that the electronic states near E_F can preexist in the insulators and are not due to a Kondo-type resonance which arises from interaction of the nearly localized Cu d^9 configuration with conduction electrons/holes with Fermi surfaces.

In order to further demonstrate the existence of split-off oxygen states in insulators, we present in Fig. 3 spectra of $Sr_2CuO_2Cl_2$ which has a K_2NiF_4-type structure consisting of CuO_2 and SrCl planes. For $h\nu = 21.2$ eV the Cl 3p photoionization cross section is greater than that of O 2p whereas for $h\nu = 40.8$ eV the Cl 3p-derived emission is suppressed owing to a Cooper minimum around this pho-

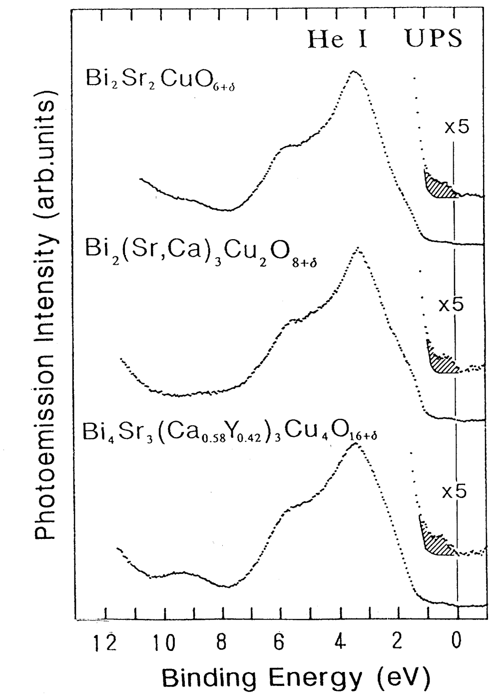

FIG. 2. Photoemission spectra of superconduction $Bi_2Sr_2CuO_{6+\delta}$ (one-CuO_2-layer) and $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ (two-CuO_2-layer, Ref. 8) and insulating $Bi_4Sr_3(Ca_{0.58}Y_{0.42})_3CuO_4O_{16+\delta}$ (two-CuO_2-layer). Shaded areas represent split-off oxygen states.

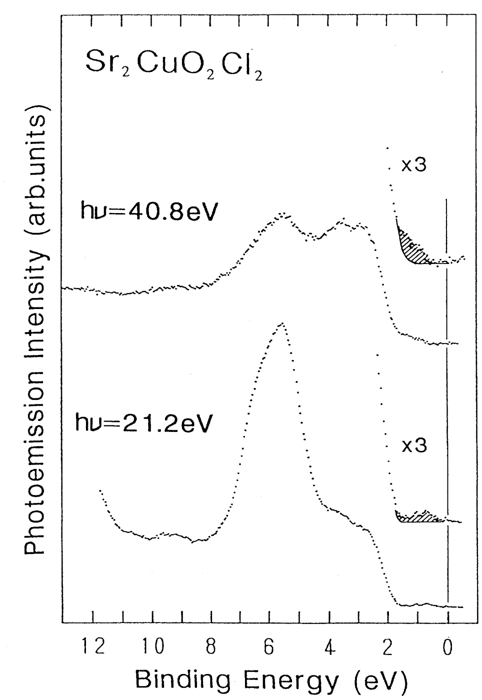

FIG. 3. Photoemission spectra of $Sr_2CuO_2Cl_2$, a K_2NiF_4-type insulator consisting of CuO_2 and SrCl planes. The 21.2-eV spectrum (bottom) is dominated by Cl 3p-derived emission while the 40.8-eV spectrum (top) by O 2p-derived emission.

ton energy, the spectrum being dominated by the O 2p partial DOS.[16] We find that the Cl 3p band is located well below E_F (centered at binding energy $E_B \sim 6$ eV) and that its contribution to the region near E_F would be small. Thus, we conclude that the weak emission above the top of the O 2p band is derived principally from oxygen p states of the CuO_2 planes. As the $Sr_2CuO_2Cl_2$ sample was free from defects at least near the oxygen sites judged from the purely single-component O 1s core-level spectrum, the split-off oxygen p states cannot be due to defects but are certainly due to Cu d^9–O 2p local singlets. (Only the local singlet $^1A_1$ is possible for the CuO_2 planes having no apex oxygens.[11,12] Thus it is tempting to speculate that the dispersive states near E_F of the Bi-Sr-Ca-Cu-O superconductors are band states derived from overlapping local singlets. Indeed, the $^1A_1$ state is consistent with the $p_{x,y}$ character of doped oxygen holes suggested by the oxygen K-edge electron-energy-loss study.[19] On the basis of these and the present experimental results, however, one cannot completely rule out the possibility that the split-off oxygen $p_{x,y}$ states in the Bi-Sr-Ca-Cu-O system are associated with the BiO or SrO planes.[8]

Here we would like to point out that the existence of split-off oxygen states in the insulators may not necessarily be a common feature of the Cu-oxide systems: For $YBa_2Cu_3O_y$, extra holes have been found to have both $p_{x,y}$ and p_z character,[19] consistent with the z^2-y^2-symmetry combination of p orbitals of the four oxygens coordinating the chain Cu(1) atoms. In this case, the number of the split-off states will increase with oxygen concentration because these states are essentially antibonding states formed between the d states of Cu(1) and the p states of excess oxygens in the chains.[14] Thus, unlike in the case of the Bi compounds, the spectra are expected to behave apparently as a function of doping as in Fig. 1(b). A recent photoemission study on YBa_2CuO_y have shown a weak emission feature near E_F with a Fermi edge for $y \sim 7$ but not for $y \sim 6$,[20] confirming the above expectation.

As for $La_{2-x}Sr_xCuO_4$, band-structure calculations have suggested that split-off states can be formed out of the oxygen p band into the charge-transfer gap upon Sr substitution because of the effectively positive charges of the Sr sites in the La_2CuO_4 host.[12,15] If this is the case, the intensity of emission near E_F is expected to increase with Sr concentration as in the case of $YBa_2Cu_3O_y$. Indeed, photoemission spectra of $La_{2-x}Sr_xCuO_4$ show no significant emission above the main p band for undoped and lightly doped ($x < 0.1$) samples[8] but show observable emission for highly doped ($x \sim 0.2$) samples.[5] A recent optical study on $La_{2-x}Sr_xCuO_4$ films[21] has shown an absorption peak below the band gap: The intensity of the absorption increases with Sr concentration, which can be naturally interpreted as due to transitions from the Sr-induced split-off oxygen states into the conduction band.

In conclusion, we have shown that the weak emission within ~ 1 eV of E_F in Cu-oxide superconductors which corresponds to Fermi-liquid states are due to states which are split off from the main O 2p band, and cannot be due to Kondo-type resonances and associated renormalized band states. For the Bi-Sr-Ca-(Y-)Cu-O system, the split-off oxygen states preexist in the insulators and might possibly be Cu d^9–O p hole local singlets ($^1A_1$) formed within the CuO_2 plane. As for the Y-Ba-Cu-O and La-Sr-Cu-O systems, the split-off states appear to be induced by excess oxygen and substituted Sr, respectively.

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