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Spectroscopic evidence for strongly correlated electronic states in La-Sr-Cu and Y-Ba-Cu oxides

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Photoemission studies of $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2Cu_3O_{6.7}$ have revealed that their electronic structure is essentially that of a Mott insulator, i.e., Cu 3*d* electrons are localized, and the density of states at the Fermi level is very low. This result combined with the magnetic properties suggest a fluctuation of the local moment due to intersite exchange, which may be consistent with a bipolaron state or a resonating valence-bond state.

Recently discovered high-T_c superconductivity in the La-Ba-Cu-O system[1] and related Cu oxides[2-4] has stimulated extensive research in these materials. So far, most theoretical studies have been based on the two-dimensional character of the electronic energy bands giving a high density of states (DOS) near the Fermi level (E_F).[5-7] Density-functional band-structure calculations[6] have yielded a strongly hybridized Cu 3*d*–O 2*p* antibonding band at E_F, which leads to a strong electron-phonon coupling for a breathing-type displacement of O atoms. On the other hand, Anderson has proposed the resonating-valence-bond or quantum-spin-liquid state,[8] which may occur in frustrated Heisenberg spin systems, and also discussed their unusual magnetic and transport properties in the normal state.[9,10] In the light of the above two extreme points of view, the knowledge of the electronic structure is a key step toward understanding not only the superconducting but also the normal-state properties. This Rapid Communication reports a photoemission study on $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2Cu_3O_{6.7}$. The results demonstrate that the Cu 3*d* electrons are essentially localized due to strong electron correlation at the Cu sites.

We have studied sintered samples of $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2Cu_3O_{6.7}$ which were prepared as described in Refs. 2 and 4 and whose properties are listed in Table I. Room-temperature x-ray and ultraviolet photoemission (XPS and UPS) experiments were performed using a spectrometer fitted with a Mg $K\alpha$ x-ray source ($h\nu = 1253.6$ eV) and a helium resonance lamp ($h\nu = 21.2$ and 40.8 eV). The energy resolution was ~0.1 eV for UPS and ~0.8 eV for XPS. The base pressure in the spectrometer was $\sim 1\times 10^{-10}$ Torr. The spectra have been corrected for the Mg $K\alpha_{3,4}$ satellite and the analyzer transmission efficiency. Clean surfaces were obtained by *in situ* scraping with a diamond file. Scraping was repeated frequently so that no change in the spectra was observed during the measurements.

Figure 1 shows XPS spectra in the Cu 2*p* core-level region, where one can see that each of the $j=\frac{1}{2}$ and $\frac{3}{2}$ components exhibits a two-peak structure as in previous reports.[11] The higher and lower binding-energy (satellite and main) peaks correspond, respectively, to $\underline{2p}3d^9$ and $\underline{2p}3d^{10}$ final-state configurations ($\underline{2p}$ denotes a Cu 2*p* core hole), so that the separation between the two peaks is approximately the intra-atomic Coulomb energy between the core hole and the 3*d* electron U_{cd}. The satellite structure arises not only from the coexistence of the $d^9(Cu^{2+})$ and d^{10} (Cu^{1+}) configurations in the ground state but also from a ligand-to-*d* charge transfer in the photoemission final state.[12] Thus the present spectra are consistent with either d^9 or a mixture of the d^9 and d^{10} configurations as the ground state. The d^8 component in the ground state would be insignificantly small in all samples, as this would given rise to $\underline{2p}3d^8$ peaks at binding energies higher than the $\underline{2p}3d^9$ peaks by $\sim U_{cd} - U_{dd} \sim 3$ eV (U_{dd} is the intra-atomic Coulomb energy between *d* electrons; for its value, see below). Weak signals at the $\underline{2p}3d^8$ binding energies may be noticed by comparison with $CuCl_2$, but these signals are found to be largely due to energy-loss satellites. The absence of $\underline{2p}3d^8$ signals for $(La_{0.75}Sr_{0.25})_2CuO_{4-y}$ may appear inconsistent with the Cu valence as large as 2.2 (Table I), but, from the energy-level scheme obtained here, it can be shown that the trivalent Cu is screened by a ligand-to-*d* charge

TABLE I. Properties of the samples, the relative intensities I_s/I_m and positions ΔE_{ms} of the satellites to the main lines for the Cu $2p_{3/2}$ core level, and the electronic structure parameters (defined in the text).

Sample	T_c (K)[a]	Conductivity type above T_c	Formal valence of Cu	ΔE_{ms} (eV)	I_s/I_m	V (eV)	Δ (eV)	n_d
$(La_{0.9}Sr_{0.1})_2CuO_{4-y}$	34	Metallic	2.1[b]	8.5	0.33	1.9	0.4	9.45
$(La_{0.75}Sr_{0.25})_2CuO_{4-y}$	· · ·	Semicond.	2.20[b]	8.8	0.21	2.4	0.7	9.49
$YBa_2Cu_3O_{6.69\pm 0.03}$	90	Metallic	2.13	8.8	0.24	2.3	0.5	9.45

[a] Defined as the middle points.

[b] Reference 14.

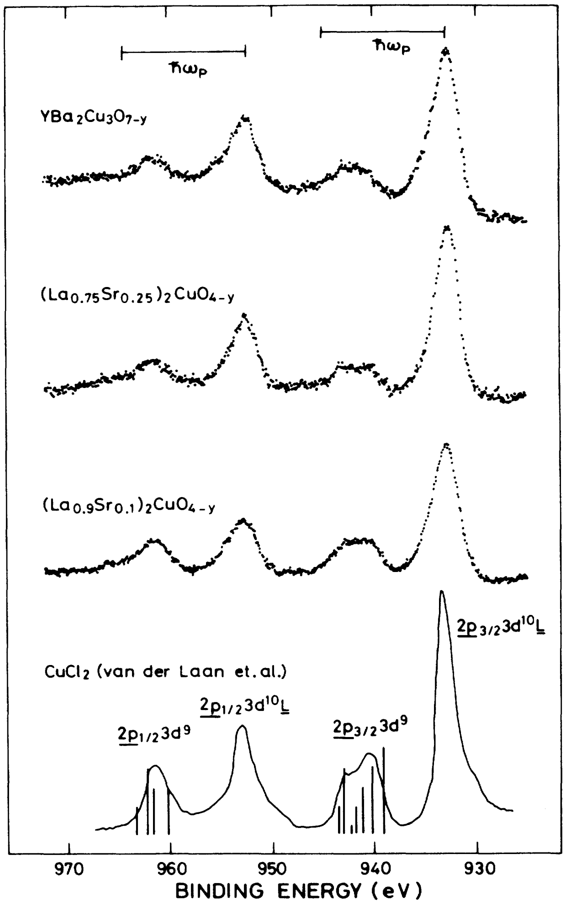

FIG. 1. Cu $2p$ core-level XPS spectra of $(La_{1-x}Sr_x)_2CuO_{4-y}$ and $YBa_2Cu_3O_{6.7}$. Also the spectrum of $CuCl_2$ is shown (Ref. 13, arbitrarily shifted to be aligned with the other spectra), for which the bar diagram of the $\underline{2p}3d^9$ multiplet is shown. $\hbar\omega_p$ represents energy-loss satellites.

transfer and becomes nearly d^9-like in its ground state. Thus, we can assume that most of the Cu sites are divalent and that the ground state is predominantly d^9, which is hybridized with $d^{10}\underline{L}$ states ($\underline{L}$ = a ligand hole) through Cu $3d$-O $2p$ covalency. Then by applying the Larsson-Sawatzky model[13] to the observed separation ΔE_{ms} and the intensity ratio I_s/I_m between the satellite and main peaks, we have evaluated the d-electron occupation in the ground state n_d, as well as the transfer integral $V \equiv \langle d^9|H|d^{10}\underline{L}\rangle$ and the charge-transfer energy $\Delta \equiv \langle d^{10}\underline{L}|H|d^{10}\underline{L}\rangle - \langle d^9|H|d^9\rangle$. Although the model assumes a cluster consisting of a Cu and ligand atoms,[13] the n_d values thus obtained are independent of the model; hence, the degree of d-electron localization. With $U_{cd}=8$ eV, we have obtained the V, Δ, and n_d values listed in Table I. These values indicate that the Cu-O bonding has considerable covalent character.

Since the main-satellite separation is approximately equal to U_{cd} and $U_{dd}/U_{cd} \sim 0.7$ for $3d$ transition-metal compounds,[15] the separation of 8–9 eV implies U_{dd} to be of the order of 5 eV. As this U_{dd} is comparable to the total band width obtained by the band calculations, the band DOS will be significantly distorted by many-body effects. In Fig. 2 we compare the valence-band photoemission spectra of $(La_{0.9}Sr_{0.1})CuO_{4-y}$ with those predicted by the band theory: Partial DOS's have been scaled with atomic-orbital cross sections[16] and broadened with instrumental resolution and lifetime width. The result indeed shows that the experimental spectral weight is considerably shifted to higher binding energies as compared to the theory and that the line shapes are quite different from each other. The agreement is even worse for $YBa_2Cu_3O_{6.7}$, for which the calculated DOS has more weight near E_F.[6] In this context, we point out that by the same procedure almost perfect agreement between theory and experiment has been achieved for the Chevrel-phase $M_xMo_6S_8$, an uncorrelated d-band metal.[17] A more serious difficulty of the band theory is that the spectra show extremely low DOS in the vicinity of E_F *both for the metallic and semiconducting samples.* Such a low DOS cannot be explained by the band theory at least for a paramagnetic state, but would be naturally explained as the opening of a Mott-Hubbard gap as a result of the strong electron correlation.

The presence of satellite features at 8–14 eV below E_F in every XPS valence band (Fig. 3) is also an indication of the strong electron correlation. Further, the $\underline{2p}3d^9$ multi-

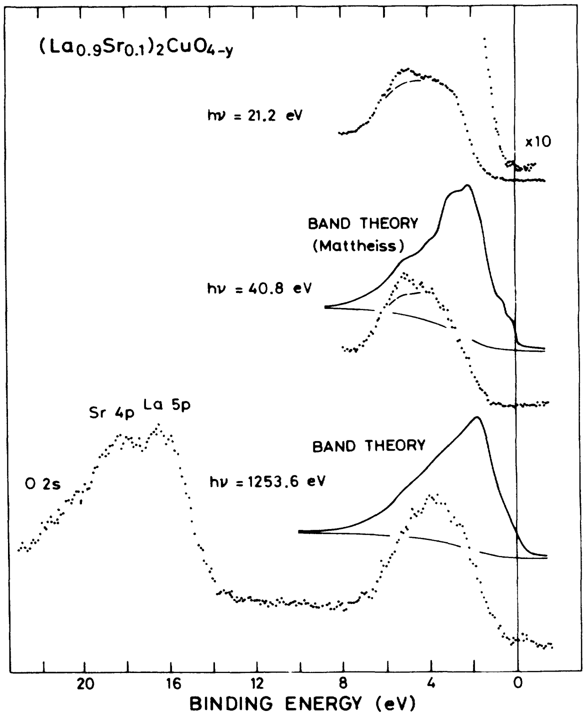

FIG. 2. Valence-band XPS and UPS spectra of $(La_{0.9}Sr_{0.1})_2CuO_{4-y}$. Spectra calculated forming the energy band DOS of Mattheiss (Ref. 6) are compared with experiment. The UPS spectra are almost identical to those of $(La_{0.75}Sr_{0.25})_2CuO_{4-y}$ except the structure at 5–6 eV below E_F as shown by dashed curves. (The extra intensity of 5–6 eV would be due to O $2p$ emission from second phases which are segregated at grain boundaries as inferred from the analysis of core levels.)

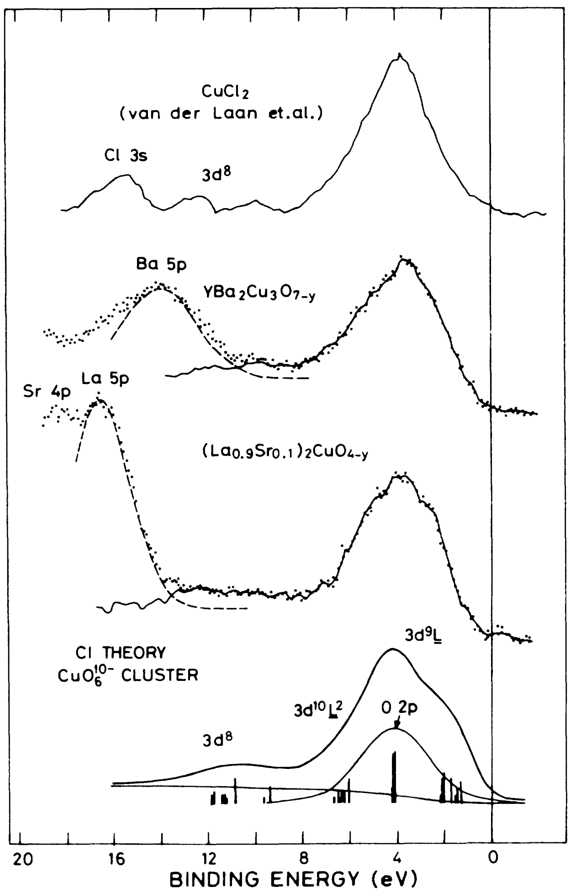

FIG. 3. Valence-band XPS spectra of $(La_{0.9}Sr_{0.1})_2CuO_{4-y}$, $YBa_2Cu_3O_{6.7}$, and $CuCl_2$ (Ref. 13) and the result of the configuration-interaction (CI) calculation for the CuO_6^{10-} cluster. Shallowest core levels (dashed lines) have been subtracted from the raw data (dots), yielding the pure valence-band contributions (solid lines).

plet structure is observable analogous to the local-moment system $CuCl_2$ (Fig. 1). This latter fact indicates that the characteristic energy scale for the fluctuation of the local moment is small enough as compared to the $\underline{2p}3d^9$ multiplet splitting of the order of ~3 eV.

In order to confirm the almost localized nature mentioned above and to get quantitative electronic structure information, we have performed a configuration-interaction calculation on a CuO_6 cluster, which takes into account the intra-atomic Coulomb and exchange interactions between d electrons and has been successfully applied to Mott insulators such as NiO and Fe_2O_3.[18] The cluster is assumed to be cubic for simplicity. (The tetragonal distortion will further split the final-state energy levels, thereby affecting the detailed spectral line shape, but would not change the relative positions of the d^8, $d^9\underline{L}$, and $d^{10}\underline{L}^2$ final states which determine the gross spectral distribution.) With the O to Cu atom ratio ~4 corresponding to $(La_{1-x}Sr_x)_2CuO_{4-y}$, the XPS valence band including the satellite region has been well reproduced by using $\Delta \simeq 0$ eV, and $U_{dd}=5.5$ eV, $(pd\sigma)=-1.1$ eV, and $(pd\pi)=0.55$ eV (corresponding to $V=1.9$ eV) as shown in Fig. 3. Much improved agreement will be obtained if we use a more realistic distorted cluster geometry and/or a complex O $2p$–band line shape,[18] and such a calculation is under way. The parameter values are in good agreement with the V and Δ obtained from the core-level analysis, considering the highly effective nature of these parameters for different spectroscopies.[15] Here, we note that as in the case of NiO (Ref. 18) the main band within ~7 eV of E_F is largely ascribed to charge-transfer-screened $d^9\underline{L}$ (and $d^{10}\underline{L}^2$) final states, and the satellite to unscreened d^8 final states. This means that the gap at E_F is not the ordinary Mott-Hubbard (d^8-d^{10}) type, but is the charge-transfer $(d^9\underline{L}-d^{10})$ type.[19]

Then, we consider the lattice of Cu atoms, which are antiferromagnetically coupled $S=\frac{1}{2}$ spins in the ground state. This usually results in antiferromagnetic ordering, but another possible ground state is a bipolaron state, which may condense into a superfluid,[20] or a resonating-valence-bond state, which may undergo a transition to a superconducting state when doped with carriers.[8] These two types of the ground states appear to be consistent with the nonmagnetic (Pauli-paramagnetic) behavior of $(La_{1-x}Sr_x)_2CuO_{4-x}$ and $YBa_2Cu_3O_{7-y}$ (Ref. 21). Finally, we note that the present study is limited by the energy resolution of ~0.1 eV, and, therefore, that structures close to E_F on a smaller energy scale may have been smeared out. Such fine structures might arise from many-body effects and play a role in the magnetic, transport, and thermal properties.

In conclusion, the present results have shown that the d electrons are almost localized as in a Mott insulator. The band model, at least that of the paramagnetic state presented so far,[6] would not be a good starting point for studying the high-T_c superconductivity mechanism. Theoretical models consistent with the strongly correlated, almost localized d electrons have to be developed.

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