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Observed trends in the x-ray photoelectron and Auger spectra of high-temperature superconductors

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X-ray photoelectron spectra and Auger-electron spectra are reported for La_2CuO_4 and $YBa_2Cu_3O_7$ in the tetrahedral and orthorhombic crystal structures; they are compared to previously reported data for Cu, Cu_2O, and CuO. These data reveal large electron-electron interaction effects. The magnitude of these interaction effects correlate with the transition temperatures of the superconducting oxides.

The recent discoveries of superconductivity above 30 K in $La_{2-x}Ba_xCuO_4$ (Ref. 1) and above 90 K in a mixed-phase Y-Ba-Cu-O compound[2] [subsequently shown to be $YBa_2Cu_3O_{7-d}$ (Ref. 3)], have generated a great interest in elucidating the electronic structure of these materials. The high-transition temperatures (T_c) and the lack of an isotope effect[4] have suggested that the electron-phonon interaction, as indicated by the conventional Bardeen-Cooper-Schrieffer (BCS) mechanism,[5] may not be dominant. Rather electron-electron interactions, such as in the "resonating valence bond" (RVB) mechanism, may dominate.[6] Recent band-structure calculations and published density of states (DOS) have provided great insight into the electronic structure of these materials.[7,8] However, the one-electron nature of the band-structure calculations does not provide much insight as to the nature of the electron-electron interactions.

Auger-electron spectroscopy (AES) is unique as an experimental tool in this regard, since the Auger line shape reflects a two-hole (or two-electron) DOS.[9] Certain satellite features in x-ray photoelectron spectroscopy (XPS) also reflect a two-hole, one-electron final state. We report Cu $2p_{1/2}$ and $2p_{3/2}$ (L_{23}) XPS and Cu $L_{23}VV$ AES data for three superconducting (SC) materials having the nominal composition La_2CuO_4 (herein called the La material), and $YBa_2Cu_3O_7$ with the tetrahedral (123-*t*) and orthorhombic (123-*o*) crystal structures. We compare these data with previously reported data[10] for Cu, Cu_2O, and CuO (herein called non-SC materials). Briefly, these data suggest the following: (1) the covalency of the Cu—O bond increases in the order CuO < La < 123-*t* < 123-*o* (i.e., proportional to T_c), (2) the localized nature of the antibonding Cu $3d$–O $2p$ σ^* band decreases with covalency, and (3) the electron-electron interaction energy in the Cu $3d$–O $2p$ σ bonding band decreases with covalency (i.e., screening increases).

The La, 123-*t*, and 123-*o* materials were prepared from the high-purity powders La_2O_3, Y_2O_3, $BaCO_3$, and CuO. These powders were mixed and calcined at 940 °C for 3 h (with an intermediate mixing), pressed into 1.2-cm-diam pellets and sintered for 12 h at 940 °C in air, reheated to 900 °C in oxygen for 3 h, and finally slow cooled at 1°/min. The 123-*t* material was air quenched from 900 °C instead of slow cooling. Structures were determined by x-ray and neutron diffraction. The superconducting T_c's were determined resistively. Table I gives the temperature for each SC material at which the resistance begins to drop with cooling, and the temperature at which the resistance drops to zero. The La material may exhibit a filamentary superconductivity below 40 K,[11] but our sample exhibited only a resistivity minimum around 29 K. The resistivity minimum is probably more representative of the bulk, which is reflected in the AES and XPS spectra. Both the AES and XPS spectra were taken with Al *Ka* excitation at room temperature with a Surface Science Laboratories Model SSX-100-03 spectrometer. The data were taken with a resolution of 0.85 eV for the Cu XPS and 1.2 eV for the AES spectra. The samples were scraped with a diamond tip within 5 min of insertion into vacuum. XPS indicates that surface adventitious carbon was present, but this is not expected to significantly alter the signal for the Cu coming from up to several layers beneath the surface.

Figure 1 and Table I show the XPS data comparisons. Note that large satellites are present in the Cu L_{23} XPS spectra except for Cu metal and Cu_2O. This is apparently because the Cu $3d$ band is filled in these two materials so that the previously identified $3d$ to $3d^*$ or σ to σ^* shake-up process, which may occur upon core excitation in CuO, cannot occur.[12] Larsson[12] has summarized the satellites observed in a large number of other systems as follows: (1) Spectra with atomic ligands typically have one satellite peak associated with L_2 and two with L_3, (2) the satellite intensity is strongest if the ligands are highly electronegative (i.e., ionic bonding), and (3) the energy separation between satellite and main peak increases with electronegativity. Table I indicates that the ionicity of the Cu—O bond must decrease (covalency increase) in the

TABLE I. Summary of the XPS and AES data for the six materials studied.

Item	Cu	Cu_2O	CuO	La	123-*t*	123-*o*
T_c (K)	...	...	...	43−29	80−70	93−91
			XPS			
$[E(\text{sat})-E(L_3)]^a$ (eV)		...	8.7 ∓ 0.3	8.5	9	9.2
$I(\text{sat})/I(L_3)$	...	...	0.58	0.49	0.43	0.37
			AES			
$I(L_3V\text{-}VVV)/I(L_3VV)$, Expt.^{b}	0.75	0.75	0.75	1.3	1.3	1.4
% of shakeup transferred to $L_3V\text{-}VVV^c$	0	0	0	77	85	100
$(E_p-E_F)^d$ (eV)	13.9	15.7	16.0	16.3	16.5	15.0
$(E_{tc}-E_F)^d$ (eV)	4.2	8.9	8.2	7.7	5.6	4.4
U_{eff} (eV)	...	...	...	2	≈ 0	≈ 0

[a] Estimated uncertainty ∓ 0.1 eV, except for the CuO result from Ref. 10.

[b] Estimated uncertainty ∓ 0.1; Cu result from Ref. 13; Cu_2O and CuO nominally the same as Cu; the SC's from Fig. 2.

[c] Estimated uncertainty for the SC's ∓ 10.

[d] Estimated uncertainty ∓ 0.3 eV.

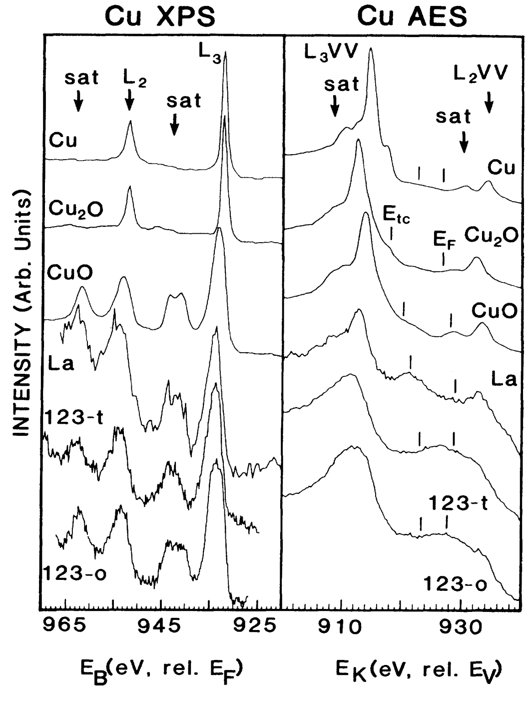

FIG. 1. Comparison of the previously published Cu L_{23} x-ray photoelectron spectra (left) and L_3VV Auger spectra (right) for Cu, Cu_2O, CuO (Ref. 10) with those obtained in this work for the superconducting materials La_2CuO_4 and $YBa_2Cu_3O_7$ in the tetrahedral and orthorhombic crystal structures (i.e., the La, 123-*t*, and 123-*o* materials). The principal components, L_2 and L_3, and satellites for each case are indicated. The vertical marks indicate the energy of the L_3 Fermi level, E_F, and the "two-center" feature, E_{tc}.

order as described above.

The $L_{23}VV$ Auger data are shown on the right in Fig. 1. Only the line shape for Cu (Ref. 10) has been quantitatively interpreted previously.[13,14] The Cu line shape has been interpreted within an atomic picture, where the final-state holes are assumed to remain on the atom with the initial core hole. The main feature at 918.8 and a smaller feature just 2.7 eV higher in kinetic energy arise from atomic multiplets within the principal L_3VV line shape; a similar main feature for the L_2VV line shape falls at 938.7 eV. Satellite features identified as arising from the $LV\text{-}VVV$ process lie just to the left of the principal L_2 and L_3 features.[13,14]

The line shapes for Cu_2O and CuO (Ref. 10) are very similar to that for Cu; however, the line shapes measured in this work for the La and 123 SC's are very different. There are two reasons for this. First, because of the Al $K\alpha$ x-ray source used in this work, the Auger line shapes of the three SC's lie on top of a large contribution arising from O 1*s* (kinetic energy = 951 eV) photoelectrons which have suffered inelastic loss processes on their way out of the sample. In a standard procedure[15] for Auger spectra, we deconvolved the entire spectrum (O 1*s* XPS plus Cu Auger region) with a backscattered electron spectrum taken such that the elastic peak had the same energy as the O 1*s* photoelectrons. This process removes most of the XPS-loss contribution as well as the Auger-loss contribution (this latter contribution is present also in the Cu, Cu_2O, and CuO spectra). These deconvolved spectra are given in Fig. 2.

Comparison of Figs. 1 and 2 reveals that the relative sizes of the satellite and principal Auger contributions in the three SC's are very different from those for the three non-SC's. To understand how this can be true, we need to

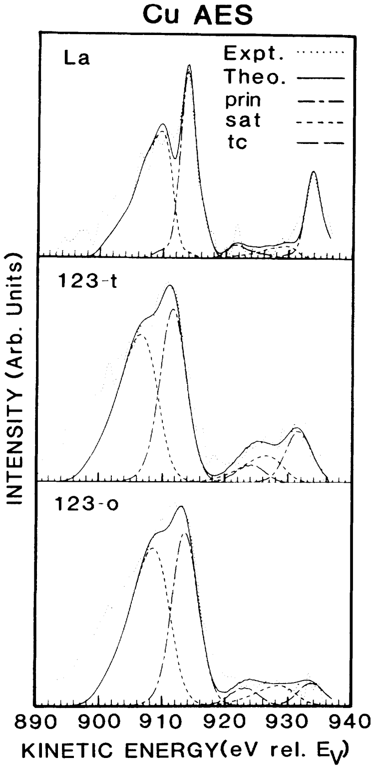

FIG. 2. Comparison of the experimental (Expt.) Cu L_3VV Auger spectra for the La, 123-*t*, and 123-*o* superconducting materials after deconvoluting out the inelastic contributions as described in the text. The theoretical line shape (Theo.) is obtained by a least-squares fit of the L_3V-VVV (sat) and L_3VV (prin) components (Ref. 14) from Cu metal as shown. These two components were broadened by Gaussians of 2 (La) and 4 eV (123) and were separated in energy by an additional 1.75 eV to obtain optimal fits. The larger broadening for the 123 materials may reflect the two different Cu sites in these materials. The two-center (tc) contribution is modeled by a self-fold of the Cu DOS (Ref. 7) after including correlation effects via the Cini-Sawatzky expression (Ref. 21) with an optimal U_{eff} as tabulated in Table I.

itemize those processes which can create the initial valence hole in the LV-VVV satellite. The relative total core ionization cross sections under Al $K\alpha$ x rays are L_1:L_2:L_3=26:54:100.[13] The L_1 and L_2 core holes may undergo Coster-Kronig (CK) decay ($L_{12}L_3V$). The resultant L_3 core hole may subsequently Auger decay, and because of the valence hole, this results in the satellite contribution. We assume that CK decay dominates for the L_1 core level, and that the level degeneracy dictates the relative final-state populations (i.e., 9 L_2V to 18 L_3V).[13,14] The relative intensities of the L_3VV and L_2VV contributions in the Cu Auger line shape are approximately L_3:L_2=5:1,[13] and hence we allot 18 to the L_2VV Auger and 36 to the L_2L_3V CK process. The theoretical probability for shakeoff of a valence electron upon "sudden" creation of a core hole in a Cu atom has been estimated to be around 10%.[16] Since this probability is nearly independent of the molecular environment,[17] we allot 10 to the L_3V-VVV satellite from shakeoff. The total L_3 ionization cross section for each material, normalized to 100, is divided among the possible L_3 processes [e.g., for CuO we have (normal:shakeup:shakeoff)=60:30:10, where the probability for shakeup is obtained from the relative intensity of the XPS satellite (Table I)]. The total satellite contribution is then 71% (i.e, {18+36+10}/{60+30}) of the principal contribution in close agreement with experiment for the non-SC's.

Table I shows that the relative satellite contribution for the three SC's is very much larger. This cannot arise from an increase of the L_2 CK decay since the experimental L_3VV:L_2VV intensity ratio in the SC's is similar to that for the non-SC's.[18] Another possibility is that some of the principal Auger intensity goes elsewhere, for example, at higher energy just below the L_2VV line shape. We do see some contribution here, but it is not any bigger than that seen in the CuO line shape, yet CuO does not show the enhanced satellite. We conclude that some intensity from the principal $L_{23}VV$ contribution must be transferred to the satellite $L_{23}V$-VVV contribution.

The transfer of principal to satellite intensity can arise from the s to s^* shakeup process discussed above. Normally, shakeup does not cause a satellite Auger contribution since the shakeup electron remains localized and thus the shakeup-Auger final state still contains only two holes.[17] However, if the s^* electron should propagate away before the core-hole decay, we then have a local three-hole state, as in the shakeoff process. We suggest that the increased intensity of the $L_{23}V$-VVV satellites for the SC's results from delocalization of the σ^* shakeup electron before the Auger decay. This does not happen in CuO, because in that material the σ^* orbital on the atom with the core and valence holes drops out of the conduction band and becomes a localized excitoniclike state with a binding energy of around 1.4 eV.[19] In the SC's no band gap exists;[7,8] however, evidence for a $3d^*$ resonance does appear in recent x-ray absorption spectra for the La material.[20] Since the XPS satellite decreases (i.e., decreasing shakeup) while the Auger satellite increases with increasing T_c in the SC's, not all of the σ^* shakeup electrons must escape before the Auger decay. The escape probability therefore must increase with covalent character, a trend one might expect as the electrons become more delocalized. Table I gives the relative amount of intensity transfer, from principal line to satellite, required to give agreement with the experimental ratio as determined in Fig. 2.

Finally, we consider the energies of the principal L_3VV feature and the feature seen in Figs. 1 and 2 between the L_3 and L_2 Auger contributions. This latter very small feature for Cu has been interpreted as a delocalized bandlike (as opposed to the atomiclike) contribution to the L_3VV Auger line shape.[13] This feature has increased intensity for the remaining oxide materials, suggesting that the larger intensity arises when one of the final-state holes is delocalized onto a neighboring O atom (i.e., an effective two-center Auger final state, but not necessarily involving a two-center Auger process). Such a final state might arise when the σ Cu—O bonding band is involved in the Auger decay, in contrast to the nonbonding or weakly π

Cu—O bonding bands which dominate the principal feature. Figure 1 and Table I show that the energy of this two-center feature relative to the Fermi level (i.e., $E_{\mathrm{tc}} - E_F$) decreases with increasing covalency. The energy of the tick marks locating the two-center contribution for the 123 materials in Fig. 1 is determined from Fig. 2. Although a two-center feature is not visible for the 123 materials in Fig. 1, as for the La and the Cu oxides, we believe a two-center contribution is still present, because the L_2 satellite cannot realistically account for all of the intensity between 920 and 930 eV in Fig. 2. We have modeled the two-center contribution in Fig. 2 for the SC's by applying the Cini-Sawatzky expression[21] to the self-fold of the Cu DOS[7] with an effective hole-hole repulsion, U_{eff}, chosen to provide optimal agreement with experiment. Table I reveals that U_{eff} decreases as the covalency increases (i.e., as T_c increases), consistent with the increased screening of the Cu-O valence holes by the more delocalized σ electrons in the covalent systems. In contrast, the σ electrons are apparently ineffective at screening the more localized holes in the π orbitals, since $E_p - E_F$ is relatively constant, except in 123-*o*. Recent calculations[7] indicate that a π^* band in 123-*o* may not be completely filled, so that in this case some of the π electrons can effectively screen the Auger π holes.

In an ionic versus covalent (i.e., local versus nonlocal) description of the bonding, we have shown that the covalency of the Cu—O bond increases with T_c. This is reflected in the intensity and energy of the XPS satellites, in the intensity of the Auger satellites, and in the effective hole-hole repulsion energies reflected in the "two-center" Auger contribution. Increased covalency usually reflects increased interorbital overlap, in this case between the Cu 3*d* and O 2*p* orbitals. This increasing 3*d*-2*p* overlap is consistent with the decreasing interatomic distances [the shortest Cu-O distance is 1.95 Å in CuO and La (Ref. 22) and 1.85 in 123-*t* and 123-*o* (Refs. 1 and 3)] and the decreasing dimensional character of the Cu-O lattice [nominally three dimensional (3D) in CuO, 2D in La and 123-*t*, and both 2D and 1D in 123-*o* (Refs. 7 and 8)] in the higher-T_c SC's. Increased covalency suggests increased mobility of the electron pairs. Electron-electron interactions dominate the Auger and XPS satellite spectra for all of these materials, and these interactions may play a significant role in the electron pair binding.[6]

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