

Synchrotron-radiation photoemission study of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Photoemission measurements have been performed on the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ using synchrotron radiation of 20–110 eV. It is found that the valence band is shifted by 1.1 to 1.6 eV towards higher binding energy relative to band calculations. The effective intra-atomic Coulomb energy between d electrons (U_{dd}) was evaluated from the energy position of the valence-band satellite due to the two-hole bound state: $U_{dd}=5\text{--}6$ eV, which is comparable to the valence-band width ($W=6\text{--}7$ eV). This strongly suggests that electron correlation plays a key role in characterizing the electronic properties of this oxide superconductor.

There has been considerable interest in the electronic structure of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 1) in connection with the mechanism giving rise to such high transition temperatures above 90 K. Mattheiss and Hamann² have calculated the band structure of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ using the linear-augmented-plane-wave method and have proposed that the large electron-phonon matrix element makes an important contribution to the observed high T_c . Similar one-electron band models have also been presented by other researchers.^{3–5} On the other hand, Anderson⁶ has proposed a nonphonon mechanism which stresses the importance of strong electron correlation. Strong Coulomb correlation has also been discussed by other researchers and is incorporated in their models.^{7–10} Although it is not finally established which mechanism, phonon or electron or both, is responsible for the occurrence of the superconductivity, the recent reports on the absence of isotope effects¹¹ seem to favor the electron mechanism. For this situation, a quantitative estimation of the effect of the Coulomb correlation in the Y-Ba-Cu-O system is necessary to get further insight into the mechanism of the high- T_c superconductivity.

In this paper we present the results of a synchrotron-radiation photoemission study of the high- T_c superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. By the use of tunability of photon energy, we have carried out resonant photoemission measurements. This technique gives us a direct measure of the intra-atomic Coulomb energy between d electrons as well as information about the chemical origin of the features in the valence band. In the resonant photoemission of the Cu $3d$ state we found a pronounced satellite

structure due to the two d -hole bound state. By analyzing the binding energy of the satellite peak, we have successfully estimated the intra-atomic Coulomb energy between d electrons (U_{dd}) as well as the chemical state of the copper atom. We discuss the obtained U_{dd} in comparison with the valence-band photoemission spectrum in order to check the validity of the one-electron-band picture in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

The sample was prepared by sintering a pressed pellet in an air and oxygen atmosphere, and its chemical composition was $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ according to the chemical analysis. The x-ray diffraction pattern was of orthorhombic form with $a=3.815$ Å, $b=3.879$ Å, and $c=11.640$ Å. Resistivity measurements of the sample showed a sharp superconducting transition temperature of 90 K.

The photoemission measurements were performed with a photoelectron spectrometer at the Photon Factory, National Laboratory for High Energy Physics, Japan. The energy resolution of the spectrometer, including that of photons, was 0.3–0.5 eV depending on the photon energies of 20–110 eV. The base pressure of the spectrometer was 1×10^{-10} Torr. In order to obtain a fresh and clean surface, the sample was scraped *in situ* just before measurement with a diamond file. Scrapping was repeated several times until almost no change was found in the spectrum. Since the sample surface deteriorates easily under ultrahigh vacuum at room temperature,¹² which may be due to removal of oxygen atoms from the surface into vacuum, the sample was kept at a low temperature [about 77 to 110 K (Ref. 13)] during scraping and measurements. We found that these experimental procedures gave a stable

and well-reproducible sample surface for photoemission measurements.

Figure 1 shows photoemission spectra for $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ measured at various photon energies. Four prominent structures, $A-D$, are observed in the binding-energy range of 0–20 eV, and furthermore, bands A and D exhibit a doublet structure. In order to study the chemical origin of each photoemission peak, we also measured constant-initial-state (CIS) spectra in the photon energies around the Cu $3p$ core threshold (about 75 eV). Figure 2 shows CIS spectra with bands $A-C$ as the initial states. The CIS spectra are normalized to the incident photon flux. As found in Fig. 2, the CIS spectrum of band C shows a distinct doublet structure at about 75 eV (denoted by arrows), while bands A_1 and A_2 show almost no prominent structures. Band B shows a slight enhancement around 75 eV. The remarkable enhancement of band C may be due to the resonance involving a two-hole bound state and the doublet structure represents the spin-orbit splitting of the Cu $3p$ core level. The observed resonant behavior of band C will be discussed later in detail.

According to the band calculation by Mattheiss and Hamann,² the first valence band (band A) consists mainly of Cu $3d$ and O $2p$ orbitals. However, as shown in Fig. 2, band A (A_1 and A_2) shows almost no resonances at the Cu $3p$ core threshold except for a very slight dent in the

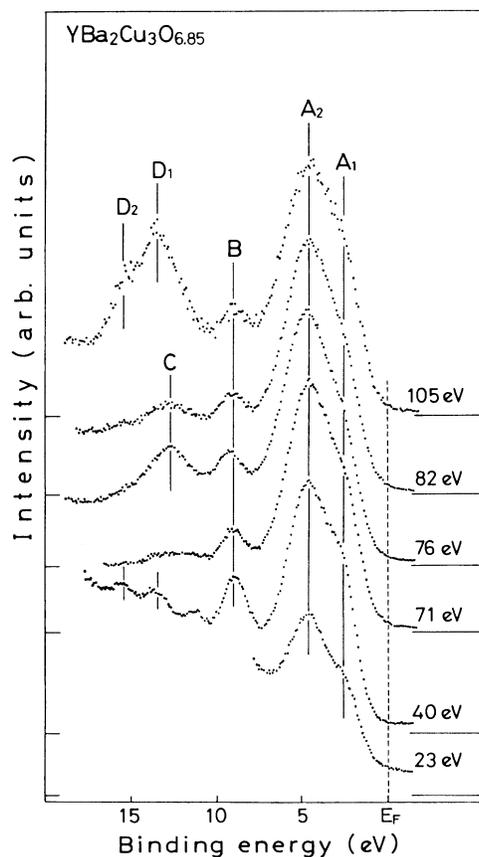


FIG. 1. Photoemission spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ measured at various photon energies. Note the resonant enhancement of band C at the Cu $3p$ core threshold ($=76$ eV).

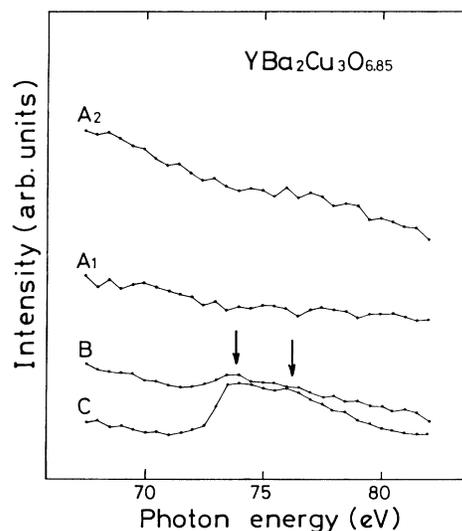


FIG. 2. Constant-initial-state spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ measured with bands $A-C$ in Fig. 1 as the initial states.

CIS spectrum of band A_1 around 75 eV. This presents a clear contrast to the cases of Cu_2O or CuO (Ref. 14), where a significant decrease ($\sim 10\%$) of the Cu $3d$ emission intensity was observed around the Cu $3p$ core threshold. In reverse, the absence of remarkable resonant behavior in band A may indicate that the hybridization of Cu $3d$ and O $2p$ orbitals is very strong in this material, as pointed out by Mattheiss and Hamann.² In the calculated total density of states, there are two prominent peaks which probably correspond to the subbands A_1 and A_2 . However, the energy positions of the two peaks in the calculation are smaller by 1.1–1.6 eV than those in the photoemission spectrum; about 1.0 and 3.5 eV in the calculation while 2.6 and 4.6 eV in the experiment. A displacement by 1–1.5 eV between calculation and experiment has been noticed already in the previous photoemission studies.^{15,16} It should also be noted that a similar discrepancy has been reported in the La-Sr-Cu-O system^{12,17,18} and has been attributed to electron correlation effects.¹⁸ This displacement remarkably affects the feature near the Fermi level. The photoemission intensity at the Fermi level is much smaller than the calculated density of states, although a small but substantial photoemission intensity at the Fermi level, which contributes to the metallic nature of this compound, is observed in the spectra.

As for band B , the chemical origin is unclear at present. Reihl, Riesterer, Bednorz, and Müller,¹⁷ reported a similar uncertain photoemission band at about 9 eV in the La-Sr-Cu-O system and ascribed it to the C $2s$ state, probably due to using SrCO_3 as a starting material. In a similar manner, band B in the Y-Ba-Cu-O system may be assigned to the C $2s$ state because BaCO_3 is used as a starting material. As shown in Fig. 2, band B shows a slight enhancement around the Cu $3p$ core threshold. This seems contradictory to the above assignment of band B to the C $2s$ state. The observed enhancement of band B , however, may be due to a tail of band C , which shows re-

markable enhancement at the Cu $3p$ core threshold and has a tail or a small subband on its low-binding-energy side.¹⁴

As shown in Fig. 1, band D shows a strong enhancement at 105 eV. Since this photon energy corresponds to the Ba $4d$ core threshold, band D is assigned to the Ba $5p$ state and the doublet structure is due to the spin-orbit splitting.

The most important finding in this study is band C , which appears only at and a little above the Cu $3p$ core threshold. In the previous synchrotron-photoemission study of $\text{YBa}_2\text{Cu}_3\text{O}_7$ by Yarmoff *et al.*,¹⁶ this band (band C) was entirely overlooked, probably because it appears in a very narrow photon-energy range (about 73–78 eV as shown in Fig. 2). Band C is assigned to a valence-band satellite due to the two d -hole bound state as observed in Ni (Refs. 19 and 20) and Cu (Ref. 21) and their compounds such as oxides.^{14,22,23} It is well established that the two $3d$ -hole bound state is produced in the final state of photoemission and its intensity is resonantly enhanced at the $3p$ core threshold owing to the interference between the direct excitation and the $3p \rightarrow 3d$ absorption followed by the super Coster-Kronig decay of the $3p$ core level.^{24,25} It has been reported²³ that the shape and the energy of the satellite depend strongly on the chemical environment such as the oxidation state and the structure of the ligand. As shown in Fig. 1, the binding energy of band C is about 13 eV, which is in good agreement with that of CuO but not with that of Cu_2O (about 15 eV).¹⁴ Further, the CIS spectrum of band C shows a close resemblance to that of CuO rather than that of Cu_2O .¹⁴ This indicates that copper atoms in orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{6.85}$ are mostly divalent. No evidence was found for the presence of Cu^{3+} oxidation state as in the previous x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) studies.^{15,16,26}

Finally, we estimate the intra-atomic Coulomb energy between d electrons (U_{dd}). If we start from the one-electron-band picture, the binding energy of the valence-

band satellite due to the two-hole bound state (E_0) is expressed as²⁵ $E_0 = 2\epsilon_d + U_{dd}$, where ϵ_d is the binding energy of the main d band and U_{dd} is the effective intra-atomic Coulomb energy. As for ϵ_d , we referred to the center of the main d band (3.5–4.0 eV) in the XPS spectrum measured in this study. Since the photoionization cross section of the Cu $3d$ orbital is much larger than that of the O $2p$ orbital in the x-ray region,²⁷ it is expected that the first valence band (corresponding to band A in Fig. 1) in the XPS spectrum represents mostly the partial density of Cu $3d$ states. Thus, we obtain 5–6 eV as U_{dd} , which is comparable to the valence-band width ($W = 6$ –7 eV, the width of band A). In general, when the intra-atomic Coulomb energy is comparable to or larger than the one-electron valence-band width, the experimental density of states is largely deviated from the one-electron-band calculation. In this sense, it is likely that the electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is considerably modified by the large correlation energy between d electrons. The observed low density of states at the Fermi level and displacement of band A between the calculation and the photoemission experiment would be due to the effect of this strong electron correlation. Although the present experimental results do not give a direct answer to which mechanism, electron or phonon, is dominant in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, it strongly suggests that a strong electron correlation plays a key role in characterizing the electronic structure of this compound. Thus, when one studies the electronic structure of the Y-Ba-Cu-O system and the mechanism of high- T_c superconductivity, the strong electron correlation has to be taken into account. A quantitative analysis of the electronic structure of Y-Ba-Cu-O system using the presently obtained parameters ($U_{dd} = 5$ –6 eV, $W = 6$ –7 eV) is urgently desired.

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