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Angle-resolved photoemission studies of single-crystal $YBa_2Cu_3O_{7-x}$

N. G. Stoffel
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701-7020

Y. Chang
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706

M. K. Kelly
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701-7020

L. Dottl and M. Onellion
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706

P. A. Morris and W. A. Bonner
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701-7020

G. Margaritondo
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706
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We present the first angle-resolved photoemission and low-energy electron-diffraction (LEED) results obtained from clean single-crystal $YBa_2Cu_3O_{7-x}$ (001) surfaces prepared by cleaving in a vacuum. The surfaces exhibit (1×1)-ordered LEED patterns, but many of the photoemission features exhibit little or no angular dependence. The most important exception is the upper spectral edge, which shows angular dispersion and a strong photon energy dependence.

Since the discovery of superconductivity at temperatures above 90 K,[1] the study of the properties of $YBa_2Cu_3O_{7-x}$ and similar compounds has been the most active area of condensed-matter research. Among these properties, the electronic structure is one of the essential ingredients of theoretical models for high-temperature superconductivity. This has stimulated a number of photoemission experiments on sintered pellets of these oxides.[2-9] To our knowledge, however, no previous experiments have explored cleaved single-crystal specimens with electron spectroscopies or electron diffraction.

Recently, we were successful in producing clean surfaces by *in situ* cleavage of single-crystal $YBa_2Cu_3O_{7-x}$, and in studying their structural and electronic properties with low-energy electron diffraction (LEED) and with angle-resolved photoemission spectroscopy. Our angle-resolved spectra avoid the orientational averaging which limits the electronic structure information available from earlier polycrystalline photoemission studies, and furthermore, should be free of the contributions, due to extrinsic materials, generally found at the mechanically exposed surfaces of the sintered samples.[10] In particular, our results reveal a photon-energy-dependent emission from states near the Fermi energy E_F which show apparent angular dispersion. Specifically, we found that for the spectra taken at low photon energies near 18 eV, the upper edge moves towards E_F for increasing values of the angle θ between the surface normal and the direction of photoelectron emission. Our results are not completely reconcilable with either the localized cluster[11] or the one-electron band theories[12-15] for high-temperature superconductors.

The preparation of high-quality single-crystal $YBa_2Cu_3O_{7-x}$ surfaces was, of course, a crucial component of these experiments. Free-growing single crystals were prepared by a partial-melt growth technique using excess CuO as a flux.[16,17] Polarized-light microscopy showed that these crystals have few (110) oxygen-ordering domain walls. The cation stoichiometry and crystalline quality of the samples were confirmed by Rutherford backscattering spectroscopy and axial channeling.[18] The superconductivity of the single crystals was characterized by ac susceptibility. The percent diamagnetism versus temperature revealed an onset of superconductivity at 90 K, with the midpoint of the transition occurring at 70 K.

Single-crystal platelets up to 2 mm in size were bonded to metal tabs and mounted flat on a sample holder of a synchrotron-radiation photoemission spectrometer with a conductive, ultrahigh-vacuum-compatible epoxy, and cleaved *in situ* under pressures in the 10^{-10} range, using a procedure similar to that reported in Ref. 19. The quality of the single-crystal surfaces obtained with this approach is demonstrated by the sharp 1×1 low-energy electron-diffraction (LEED) patterns. Some of the LEED pictures are shown in Fig. 1. These patterns show that the cleavage surface is perpendicular to the c axis, and clearly reflect the nearly square two-dimensional Brillouin zone with very similar primitive reciprocal lattice vectors, $2\pi/a \sim 1.62$ Å^{-1} and $2\pi/b \sim 1.64$ Å^{-1}.

Angle-resolved photoemission spectra were taken on crystals excited by monochromatic synchrotron radiation from a Seya-Namioka monochromator, using a Vacuum

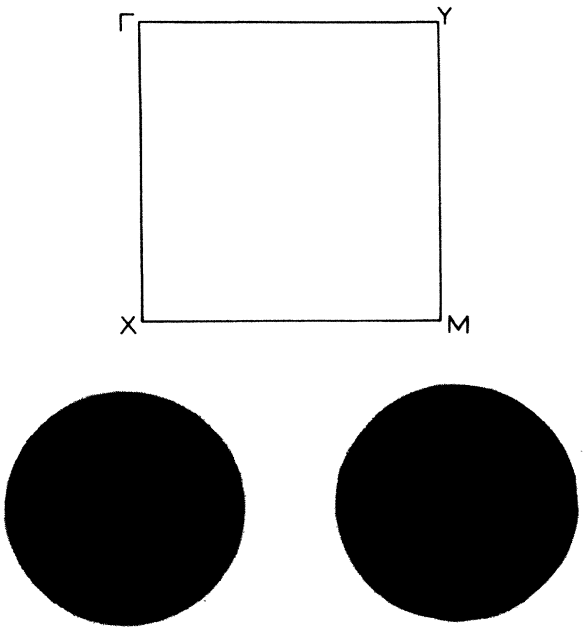

FIG. 1. LEED patterns taken with an incident electron energy of 66 and 67 eV on cleaved surfaces obtained from two different $YBa_2Cu_3O_{7-x}$ single crystals. These patterns reflect the two-dimensional projection of the Brillouin zone (top).

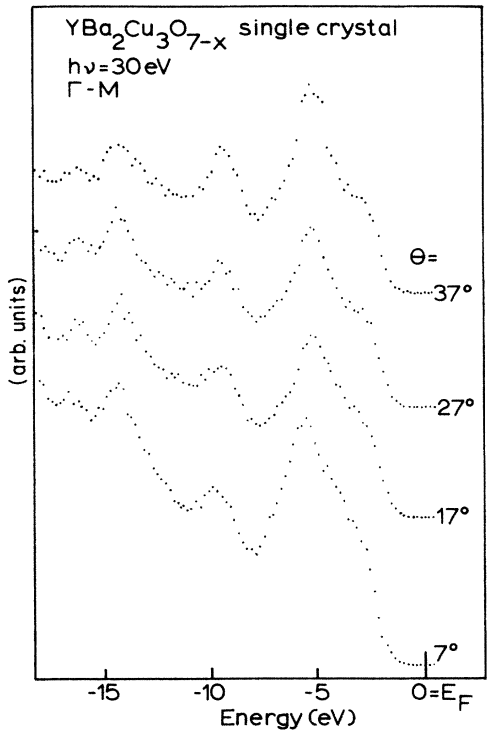

FIG. 2. Angle-resolved photoemission spectra of single-crystal $YBa_2Cu_3O_{7-x}$, taken at $h\nu=30$ eV, at the indicated angles θ from the surface normal, and at an azimuthal angle corresponding to the Γ-M direction in the two-dimensional Brillouin zone.

Science Workshop hemispherical electron energy analyzer.[20] The typical overall resolution of the spectra was 0.22 eV. The normal-emission direction was determined from the reflection angle of a He-Ne laser. The crystal orientation was confirmed by LEED only after the photoemission studies were completed, since electron beams have been found to affect surface oxygen stoichiometry. Results presented in this paper were obtained only on samples which cleaved across the entire width of the a-b plane, as confirmed by microscopic examination. Typically, about 90% of the cleaved surface appeared to be specularly reflecting (001) planes. Uncleaved portions of the crystal platelets were easily distinguishable by microscopic examination, and partially cleaved crystals yielded weak and degraded photoemission spectra. No evidence for modification of the photoemission spectra was observed over periods of the order of a day.

Figure 2 shows several angle-resolved photoemission spectra taken at a photon energy $h\nu=30$ eV, and at a different values of the angle θ between the photoelectron emission direction and the normal direction. The projection of the emission direction in the cleavage plane was close to the Γ-M direction of the two-dimensional Brillouin zone. In particular, spectra taken at $\theta=0$ correspond to the Γ point, i.e., to the center of the Brillouin zone. These spectra exhibit several features analogous to those observed in angle-integrated spectra obtained from sintered materials, confirming the overall validity of those data. Note, in particular, the emission from the strongly hybridized Cu $3d$ and O $2p$ orbitals, consisting of a main peak at -5.1 eV and a shoulder at -2.5 eV. Also, note the sharp Ba $5p$ doublet 14–16 eV below E_F, indicating a uniform barium valence state at the cleaved surface.

The definite presence of the peak at ~ -9.5 eV is particularly important, since many authors have attributed it to carbon contamination due to grain boundaries in sintered compounds or to other contaminants. We emphasize that this spectral feature is intrinsic to clean single crystals. We have also observed this feature on polycrystalline samples grown from nitrides rather than from carbonates.

The spectra of Fig. 2 exhibit little or no dispersion of the main photoemission peak, of the peak at -9.5 eV and, of course, of the Ba $5p$ doublet. These findings are not surprising, considering the results of one-electron band-structure calculations. In essence, all such calculations[12–15] give similar results, with a large number of bands with little dispersion appearing in the energy range of the main Cu-O peaks. In general, the only states with notable dispersion are made up of $pd\sigma$ bonding and antibonding orbitals. These states are essentially nonbonding at the zone center, leading to a narrow predicted bandwidth near Γ. Calculations shows these bands dispersing away from the main nonbonding bands as the electron wave vector moves towards the zone boundary. Thus, the one-electron band description predicts that four of the 36 Cu-O bands will cross or approach the Fermi level as the photoelectron detector angle is moved off the normal direction.

Despite this prediction, the region within 1 eV of E_F is remarkably free of photoemisison signal for 30 eV photon energy, as seen in Fig. 2. In contrast, a substantial photoyield is seen near E_F for lower photon energies, e.g., 18 eV. In Fig. 3, we compare spectra for 18- and 25-eV photon energies after aligning the Fermi levels and scaling the spectra to the same height of the main feature. Spectra taken at 18 eV for different values of the angle θ are shown in Fig. 4. As seen in this figure, the leading edge of the upper feature is below E_F for normal or near-normal emission whereas, considering the instrumental broadening, it coincides with E_F at larger θ angles. The leading edge position as a function of the photoelectron k-vector component parallel to the surface exhibits an upwards shift of 0.25–0.3 eV on moving from the Γ point of the two-dimensional Brillouin zone to a point approximately 75% of the way of the corner of the zone at M. Such a dispersion is larger than the uncertainty of ± 0.1 eV.

The interpretation of these angular effects is directly affected by the choice of the theoretical framework for the electronic structure of these materials. There are, at present, two extreme theoretical approaches to the problem. One is based on the standard one-electron band theory wherein electron-electron correlation is neglected or only treated approximately. The other considers the correlation, particularly between the Cu $3d$ electrons, as the dominant energy in the system. This latter approach typically involves calculating the energy levels of isolated molecular clusters in a configuration-interaction scheme, and ignoring the delocalized continuum in which these clusters may be imbedded. Spectroscopic measurements of multihole final states have shown that the correlation energies of the Cu $3d$ electrons are important in $YBa_2Cu_3O_{7-x}$.

Data such as ours provide a stringent test for the relative merits of these two approaches, which could not be provided by earlier angle-integrated photoemission data. In general angle-dependent spectra are most easily interpreted within the one-electron band picture, since dispersion is difficult to handle in the localized cluster approach. In fact, some features of our angle-dependent spectra could be explained by one-electron band-structure theories.[12-15] In particular, such theories predict, in the energy region near E_F, a group of $pd\sigma$ antibonding bands. These bands exhibit a similar, strong upwards dispersion on going from the Γ point of the zone boundary. This leaves a gap at the Γ point, in agreement with our data. The shift in energy of the leading spectral edge, observed for example in Fig. 4, is qualitatively consistent with the dispersion of the one-electron $pd\sigma$ bands.

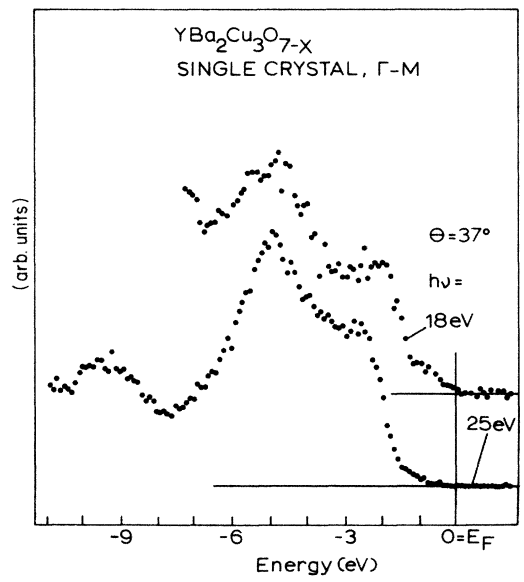

FIG. 3. Comparison of the $h\nu = 25$ and $h\nu = 18$ eV photon energy spectra at $\theta = 37°$. Note the emission close to E_F in the latter case.

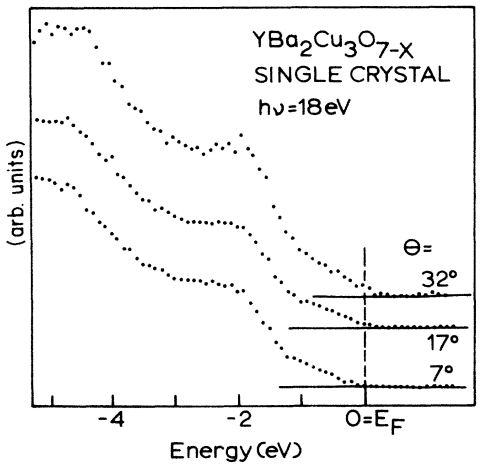

FIG. 4. Angular dependence of the spectra taken at $h\nu = 18$ eV.

On the other hand, some other features in our data are not immediately explained by one-electron pictures. For example, the *quantitative* dispersion suggested by the shift of the leading edge appears smaller than that of the calculated one-electron upper bands. The calculated dispersion is, in fact, of the order of 2 eV on going from the Γ point to the M point.

The intensity of the photoemission signal close to E_F also raises interesting questions. The fact that we did observe, in some spectra, signals all the way up to E_F is very important—in particular, it rules out the possibility of explaining the discrepancies between calculated one-electron density-of-state curves and angle-integrated photoemission spectra as a simple rigid shift. However, the relative intensity of the observed signal is always below the level suggested by one-electron calculations.

Even assuming that a one-electron picture is valid, the complexity of these compounds makes it impossible to produce a detailed band-structure mapping of all bands by angle-resolved photoemission. Our experiments, however, did reveal important angular effects involving the states near E_F. The corresponding data provide a stringent test for any treatment of the electronic structure high-temperature superconductors. Further experiments are underway to examine other aspects of the occupied and unoccupied electron states of single-crystal $YBa_2Cu_3O_{7-x}$.

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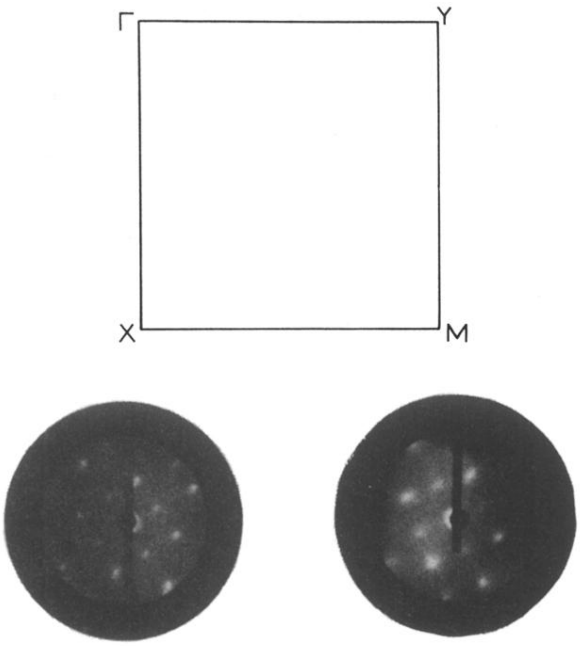

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