RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 7 1 MARCH 1989

Angle-resolved photoemission spectra of single-crystal $Bi_2Sr_2CaCu_2O_x$

F. Minami and T. Kimura
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060, Japan

S. Takekawa
National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki 305, Japan

(Received 3 October 1988; revised manuscript received 28 November 1988)

Angle-resolved photoemission measurements have been made on the recently discovered high-T_c superconductor $Bi_2Sr_2CaCu_2O_x$. From the results, E vs $k_{\parallel}$ dispersion curves have been obtained along two principal symmetry directions in the two-dimensional Brillouin zone. Compared to results of one-electron band calculations, the observed bands are shifted and distorted by strong correlation effects. One band intersects the Fermi level. This band is assigned to the renormalized "heavy-electron" band.

Since the discovery of high-T_c superconductivity in layered copper-oxide compounds, the study of the properties of these compounds has become an exciting research area. Among the properties, the knowledge of the electronic structure is especially important to understand the mechanism of high-T_c superconductivity. This has stimulated a number of photoemission experiments on sintered and single-crystal specimens of these oxides.[1] It is now widely believed that electron correlation is quite important in these systems and that the Mott-Hubbard picture is more appropriate than the band picture to describe the electronic structure of these materials.[2] However, recent photoemission studies have revealed that some features of angle-dependent spectra can be explained by one-electron band calculations.[3,4] In this Communication, we study angle-resolved photoemission spectra of the recently discovered $Bi_2Sr_2CaCu_2O_x$ (Ref. 5) and check the applicability of one-electron band theory. The experimental results indicate that the occupied electronic states near the Fermi edge have dispersion but do not coincide with "bare" bands calculated by one-electron band theory.

Single crystals of $Bi_2Sr_2CaCu_2O_x$ were grown by the floating-zone method.[6] The well-developed surface was the (001) plane and it was also a cleavage plane. The structure was indexed on an orthorhombic (pseudotetragonal) subcell with space group $Fmmm$ (D_{2h}^{23}) and lattice parameters $a \approx b = 5.43$ Å and $c = 30.63$ Å. (The Brillouin zone of this compound is shown in Fig. 1.) An incommensurate modulation of small amplitude seems to occur in the Bi-O subsystem. The structural anisotropy associated with this superstructure has recently been observed by us using Raman scattering.[7] This anisotropy is also reflected in the azimuthal dependence of the angle-resolved photoemission data. Details of this dependence will be published in a separate paper. The resistivity measurements showed that our samples have T_c of ≈ 86 K and a transition full width of ≈ 10 K.

Photoemission measurements were performed in an ultrahigh-vacuum electron spectrometer (VG model ADES 400), in which the electron energy analyzer can be rotated to vary the polar angle θ of photoemission from the sample. The azimuthal angle ϕ was kept constant at $\phi = 0°$ and 45°, which correspond to the ΓX and $\Gamma \bar{M}$ directions in the Brillouin zone, respectively. The energy resolution was ≈ 0.2 eV and the angle resolution $\approx 2°$. Single crystals ($\approx 4 \times 10 \times 1$ mm^3) were cleaved in a vacuum of $\approx 1 \times 10^{-10}$ Torr. The cleavage (001) surface was smooth and optically specular. No changes in uv photoemission spectra were observed during one cycle of measurements of ≈ 20 h. After ≈ 48 h, some changes were observed around ≈ 5 eV binding energy (cf. Fig. 2). The changes would be caused by contamination. All spectra were taken by using He I photons ($\hbar\omega = 21.2$ eV). The photon incident angle, measured from the surface normal, was kept constant at 45°. The detection angle θ (again measured from the surface normal) was varied $-15°$ to $+75°$ in step of 2°.

A number of representative spectra for the ΓX and $\Gamma \bar{M}$ directions are shown in Fig. 2. The curves are plotted with respect to binding energy E_B, taking the zero of energy at the Fermi level E_F. No background subtraction has been applied. These spectra exhibit several features analogous to those observed in angle-integrated spectra of $Bi_2Sr_2CaCu_2O_x$ and other high-T_c Cu oxides: a main peak at ≈ 4 eV and a weak photoemission intensity near the Fermi level.[1,8] In contrast to the case of $YBa_2Cu_3O_{7-x}$, however, a clear Fermi edge is observed in this ma-

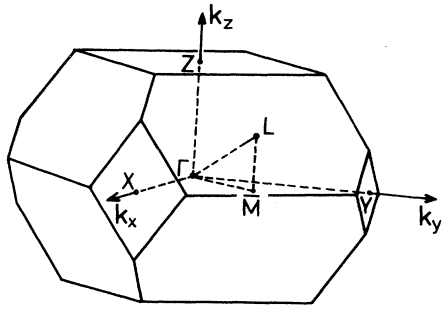

FIG. 1. Brillouin zone for the face-centered orthorhombic Bravais lattice: $X = 2\pi\,(1/a,0,0)$, $\bar{M} = \pi\,(1/a,1/b,0)$.

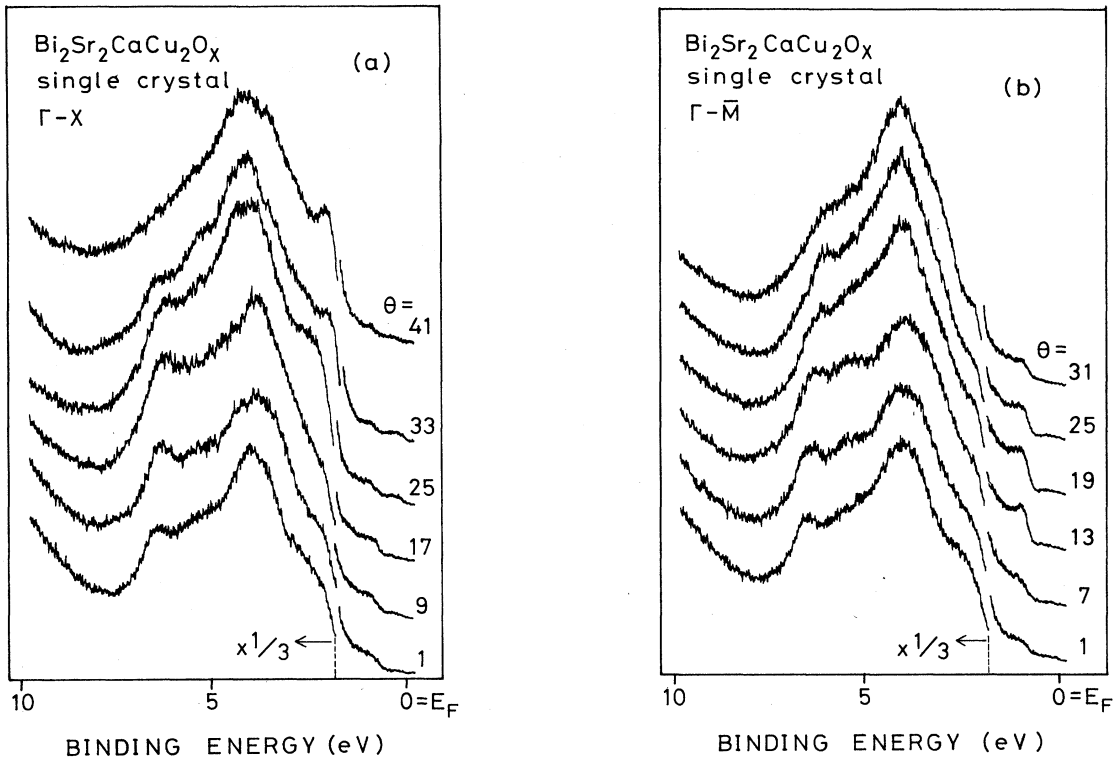

FIG. 2. Polar angle dependence of photoelectron spectra for the ΓX and $\Gamma\bar{M}$ directions with $\hbar\omega = 21.2$ eV.

terial. This is visible for example in the spectrum at $\theta = 33°$ for the ΓX azimuth. The peaks and shoulders in the energy range between 0 and 8 eV are considered to be attributable mainly to emission from the strongly hybridized Cu $3d$ and O $2p$ orbitals.[1,2,8–12] Band calculations on $Bi_2Sr_2CaCu_2O_8$ also predict that there is a contribution from Bi $6p$–O $2p$ states in this energy range. The positions of these peaks are changed largely within an angular range of about 40°. The width of the main peak at ≈ 4 eV varies markedly with θ. This indicates that this peak is composed of some bands with slightly different energy and dispersion. The spectra also show large angular change in peak intensity. In this Communication, however, we confine ourselves to the angular variation of peak positions. A discussion of the change in peak intensities will be given elsewhere.

Angle-integrated photoemission spectra of high-T_c materials were interpreted comparatively well in terms of the local cluster model.[2] In this approach, however, dispersion is difficult to handle. Here we compare our data with the one-electron band calculations by mapping the energy bands from the angle-dependent spectra. To obtain the two-dimensional band structure from the data, we adopted the usual procedure.[13] From each peak or shoulder in the spectra, we read off the kinetic energy E_k in vacuum through the relation $E_k = \hbar\omega - W - E_B$, where W is the ionization potential. The parallel wave vector $k_\parallel$ corresponding to each of these values for E_k, was evaluated from the relation

$$k_\parallel = (2mE_k/\hbar^2)^{1/2}\sin(\theta) . \quad (1)$$

We then plotted the initial energy $E_i = -E_B$ against $k_\parallel$. The results obtained for the $\Gamma\bar{M}$ and ΓX azimuths are shown in Fig. 3. From the photothreshold measurements, the ionization potential W was estimated as 4.8 eV. The points X and $\bar{M}$ on the first Brillouin-zone boundary occur at wave vectors of ≈ 1.16 and ≈ 0.82 Å^{-1}, which correspond, respectively, to angles of $\approx 33°$ and $\approx 23°$ for states just below the Fermi edge. The data then extend beyond the first Brillouin-zone boundary. For the ΓX azimuth the corresponding trajectory in the $k_z = 0$ plane is $\Gamma X\Gamma$, so that we observe mirror symmetry about the X point. The experimental spectra indeed display such mirror symmetry around $\theta \approx 33°$. The reduced data from higher Brillouin zones to the first zone are not presented in the figure.

The energy bands in $Bi_2Sr_2CaCu_2O_8$ have been calculated from first principles by several workers.[9–12] The results of these calculations are essentially the same. Here we compare our results to the energy bands by Massidda, Yu, and Freeman.[11] The calculated electronic structure shows a strong two dimensionality (dispersion along z direction being less than 0.1 eV for most occupied bands). The full lines in Fig. 3 refer to the calculated energy bands along ΓX and $\Gamma\bar{M}$ directions. Two different types

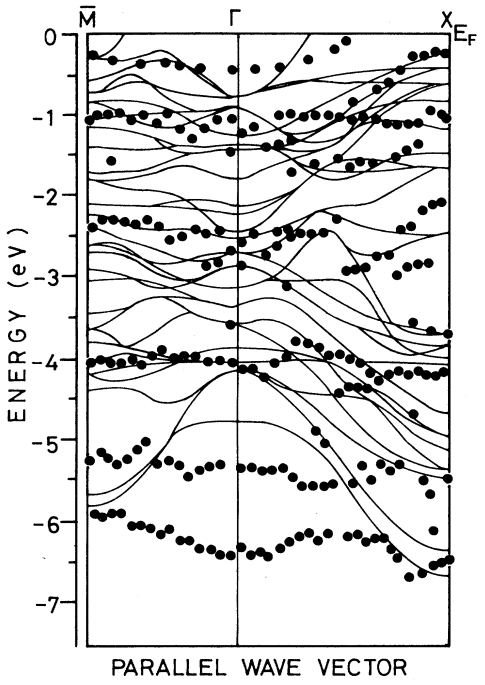

FIG. 3. Peak positions vs $k_{\parallel}$. Circles stand for peaks or shoulders in the experimental spectra. The solid lines refer to the calculated energy bands in the $k_z=0$ plane of the Brillouin zone. The band calculation used here is that of Massidda, Yu, and Freeman (Ref. 11).

of bands intersect E_F. The first corresponds to a nearly degenerate pair of antibonding Cu $3d$-O $2p$ ($dp\sigma$) states that disperse above E_F toward the X point. The second represents the lowest pair of bands from the Bi $6p$-O $2p$ ($pp\sigma$) orbitals that intersect E_F near $\bar{M}$ and form electron pockets around this point. The other bands with notable dispersion are the ones which lie about 5 eV below E_F at Γ and disperse downward away from Γ. These are made up of Cu—O $dp\sigma$ bonding orbitals. The remaining bands are composed of the Cu-O $dp\pi$, the out-of-plane Cu-O $dp\sigma$, and the Bi-O states.

Observed bands are compared to the theoretical ones in three different energy ranges. Deep bands lying 3–8 eV below E_F exhibit little or no dispersion. By upward rigid shift of ≈ 1 eV, these nondispersive bands move to the peaks of the calculated density of states. For bands between -1 and -3 eV, we can find significant indications of the dispersion. Each observed band seems to correspond to one of the theoretical bands if it is shifted again by ≈ 1 eV to higher energies. In the energy range -1–0 eV, there is a band which crosses E_F on going to X. For this shallow band, two different explanations would be possible. One is the emission from the Cu $3d$-O $2p$ ($dp\sigma$) antibonding bands whose position is almost unshifted relative to the calculated ones. The suppression of band dispersion could be attributed to correlation effects. The other is the emission from "heavy electrons" described below. We think that the latter assignment is more reasonable because the signal near E_F is only 2%–3% of the main peak signal, and certainly weaker than that predicted by the one-electron band theory. Around $\bar{M}$, we are unable to discern a feature corresponding to the electron pockets in the Bi $6p$-O $2p$ bands. Consequently, the volume of the electron pockets could be considered to be zero or much smaller than that predicted by the band calculation. On the other hand, the point at which the shallow band crosses E_F is situated about the midpoint of the ΓX direction, and closer to X than expected from the band theory. This result suggests that the volume of the Fermi surface in this material might satisfy the Fermi surface sum rule.[14] To confirm this, we are now performing Fermi surface measurements using positron annihilation.

Recently, the formation of "heavy electrons" has been predicted by an auxiliary-particle treatment of the Hubbard model,[15] which is similar to f electron systems such as $CeCu_2Si_2$ and UBe_{13}.[16] In the absence of correlation, the chemical potential is at the center of the Cu $3d$-O $2p$ ($dp\sigma$) antibonding bands in nearly half-filled cases. The bandwidth is nearly the same as the bare bandwidth even in the presence of strong correlation, although the band is highly distorted due to correlation. The chemical potential is at the top of the distorted antibonding bands. Therefore, one can expect the upward shift of the chemical potential or the downward shift of the antibonding bands. Furthermore, additional narrow bands are predicted at the chemical potential, which are the consequence of the formation of quasiparticles or "heavy electrons" due to strong correlation.

By such a theory, the shallow bands could be interpreted as follows. The band lying ≈ 1.2 eV below E_F at Γ with upward dispersion on going to X is assigned to the Cu $3d$-O $2p$ antibonding bands, which are distorted and shifted. The band lying around E_F with similar dispersion is assigned to its renormalized "heavy-electron" bands. The mass enhancement factor is evaluated to be 2–4. According to the theory, "heavy-electrons" are composed of Cu $3d$ electrons as well as O $2p$ electrons. On the other hand, from the results of resonant photoemission measurements, Takahashi *et al.* stressed that "heavy electrons" are mainly made up of O $2p$ electrons.[4] Any definite conclusion cannot be obtained about this point from our results. We think that the mechanism of enhancement in the photoemission probability for the "heavy-electron" band should be clarified to settle this problem.

In conclusion, we have studied the electronic structure of the $Bi_2Sr_2CaCu_2O_x$ by mapping the two-dimensional energy bands from angle-resolved photoemission spectra. One band intersects E_F. We suggest that this band is attributable to "heavy electrons" formed by strong correlation effects. For bands less than 3 eV below E_F, a good correspondence is found between experiment and theory, if the calculated bands are shifted by ≈ 1 eV to higher binding energies. Bands with higher binding energies have no dispersion and are not described by conventional band theory.

We thank Professor F. Ohkawa and Dr. A. Yamanaka for valuable discussions.

[1]G. Wendin, J. Phys. (Paris) **48**, C9-1157 (1988).
[2]A. Fujimori, E. Takayama-Muromachi, and Y. Uchida, Solid State Commun. **63**, 857 (1987).
[3]N. G. Stoffel, Y. Chang, M. K. Kelly, L. Dottl, M. Onellion, P. A. Morris, W. A. Bonner, and G. Margaritondo, Phys. Rev. B **37**, 7952 (1988).
[4]T. Takahashi, H. Matsuyama, H. Katayama-Yoshida, Y. Okabe, S. Hosoya, K. Seki, H. Fujimoto, M. Sato, and H. Inokuchi, Nature (London) **334**, 691 (1988).
[5]H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).
[6]S. Takekawa, H. Nozaki, A. Umezono, K. Kosuda, and M. Kobayashi, J. Cryst. Growth **92**, 677 (1988).
[7]A. Yamanaka, T. Kimura, F. Minami, K. Inoue, and S. Takekawa, Jpn. J. Appl. Phys. **27**, L1902 (1988).
[8]M. Onellion, M. Tang, Y. Chang, G. Margaritondo, J. M. Tarascon, P. A. Morris, W. A. Bonner, and N. G. Stoffel, Phys. Rev. B **38**, 881 (1988).
[9]M. S. Hybertsen and L. F. Mattheiss, Phys. Rev. Lett. **60**, 1661 (1988).
[10]H. Krakauer and W. E. Pickett, Phys. Rev. Lett. **60**, 1665 (1988).
[11]S. Massidda, J. Yu, and A. J. Freeman, Physica C **52**, 251 (1988).
[12]F. Herman, R. V. Kasowski, and W. Y. Hsu, Phys. Rev. B **38**, 204 (1988).
[13]N. V. Smith and M. M. Traum, Phys. Rev. B **11**, 2087 (1975).
[14]J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).
[15]F. Ohkawa (unpublished).
[16]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984).