Fermi Surfaces of $YBa_2Cu_3O_{6.9}$ as Seen by Angle-Resolved Photoemission

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We have carried out angle-resolved photoemission spectroscopy on single crystals of $YBa_2Cu_3O_{6.9}$. The crystals were cleaved *in situ*, under ultrahigh vacuum while the sample stage was cooled to 8 K. By observing the dispersion of the electron energy bands as they cross the Fermi energy, we have mapped the Fermi surfaces. There is reasonable agreement between the experimental results and the predictions of band-structure calculations using the local-density approximation.

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The new high-temperature superconductors with $T_c > 30$ K have in common CuO_2 planes. Therefore, many theoretical models have proposed that their electronic structure should be similar to that of (doped) $3d$ binary oxides. Since it is well known that the electrons in copper oxide are strongly correlated, those oxides might perhaps be best described by the Anderson Hamiltonian,[1] by some variant of the Hubbard model,[2] or by the resonating-valence-bond model.[3] On the other hand, if the doping is large, then superconductors such as $YBa_2Cu_3O_{6.9}$ might have enough carriers to provide significant screening, and their ground-state electronic structure might be well described by band-structure calculations using the local-density approximation (LDA). Several such calculations have been carried out for the new high-T_c superconductors.[4-6] They predict that the Fermi surfaces enclose a significant fraction of the Brillouin-zone (BZ) volume consistent with Luttinger's theorem.[6] On the other hand, current theories which treat the Cu $3d$ electrons as highly correlated predict very different (or vanishing) Fermi surfaces, particularly for small doping.[7] However, there are also indications that a moderately doped Hubbard model will yield a Fermi surface satisfying Luttinger's theorem, which is presumably the same as that predicted by LDA.[8] Therefore, an experimental determination of the Fermi surface would provide crucial guidance to a correct theoretical description of $YBa_2Cu_3O_{6.9}$.

Early angle-integrated and angle-resolved photoemission and inverse-photoemission experiments[9] have shown spectra characteristic of oxides, with a pronounced gap of ~ 2 eV in the density of states in the region of the Fermi energy. These measurements reinforced the idea that the ground-state electronic structure of the high-T_c superconductors cannot be described by a local-density approximation. However, we have recently shown that these early experiments measured samples which are not representative of bulk superconductors.[10] The surface region of $YBa_2Cu_3O_{6.9}$ undergoes rapid changes when subjected to a vacuum environment at room temperature. We have shown clear evidence of the relationship between oxygen content and density of states at E_F.[11] From x-ray-absorption spectroscopy[12] we can conclude that those changes are due to oxygen loss. This has very important consequences in photoemission spectroscopy because the mean free path of low-energy electrons in solids is very short, such that in oxygen-deficient samples a nonsuperconducting region of only a few unit cells in depth is sampled.

But if $YBa_2Cu_3O_{6.9}$ is first cooled to below 40 K and then cleaved *in situ* to reveal a fresh surface, the loss of oxygen will be considerably reduced, and the surface thus obtained will indeed be representative of the bulk.[10,11] Under such conditions, samples show a large density of states at the Fermi energy.

In most three-dimensional materials it would be exceedingly difficult to determine the Fermi surface by angle-resolved photoemission, because at a given k_x and k_y, many values of k_z may be present simultaneously in the spectrum. But in these experiments nature is on our side, since the high-temperature superconductors are nearly two-dimensional materials, and there is little or no dependence of the band energies on k_z.[5]

We use crystalline samples of $YBa_2Cu_3O_{6.9}$ which have transition temperatures above 90 K and very sharp superconducting transition temperatures (< 0.4 K), as determined by the Meissner effect. The samples are twinned, and therefore it is not possible for us to distinguish between the Γ-X and Γ-Y directions. In comparing theory with experiment we have reflected both the theoretical curves and the experimental data about the Γ-S direction in the Brillouin zone.

The experiments were carried out at the Aladdin Synchrotron (Stoughton, Wisconsin), using an extended-range Grasshopper monochromator, at a photon energy of 50 eV with a total experimental resolution of 100 meV. The angular resolution of the electron energy analyzer is $\pm 1.4°$, although experimentally, significant

shifts in the centroids of the peaks can be observed for changes of analyzer angles of only 0.5°. Thin single-crystal platelets (of typical dimensions $1\times1\times0.5$ mm^3) were mounted with epoxy glue between two Al rods, one attached to the cryostat, the other free standing, both of which were oriented along the c axis. This assembly was coated with graphite powder to ensure electrical contact. The samples were cleaved *in situ* (with the c axis normal to the sample surface) after cooling the sample holder to 8 K, by prying on the free-standing Al rod. The alignment of each sample is determined by photoemission, by observing the symmetry of the features as a function of $\mathbf{k}_\parallel$ around Γ, which leads to an accuracy of 0.5°. The results presented here have been obtained from more than a dozen samples, showing remarkable reproducibility.

Figure 1 shows energy distribution curves (EDC's) obtained along the Γ-X,Y direction at intervals of 0.115 Å^{-1}. A peak (labeled 1) can be seen dispersing as a function of $\mathbf{k}$. At $\mathbf{k}_\parallel=(0,0.35)$ Å^{-1} the peak becomes highly asymmetric, as part of it is cut off by the Fermi-Dirac distribution as the peak disperses through the Fermi energy. A peak at lower binding energy (labeled 2) can also be seen dispersing upwards. On increasing the parallel momentum further by just 0.115 Å^{-1}, to $\mathbf{k}_\parallel=(0,0.46)$ Å^{-1}, the intensity near E_F is lost. For comparison, we also reproduce the spectrum at $\mathbf{k}_\parallel=(0,0.35)$ Å^{-1} (crosses) on top of the spectrum at $\mathbf{k}_\parallel=(0,0.46)$ Å^{-1} (dots). It is clear that the band labeled 1 has crossed the Fermi level, and another band can be seen at $\sim$150 meV below E_F. Figure 1 also shows the large shift in energy of the peaks: Peak 1 has shifted in energy by more than 0.2 eV, while peak 2 has moved by more than 0.3 eV, for a change of momentum of 0.23 Å^{-1}.

Similar Fermi-level crossings can be detected at other points in the BZ. Figure 2 shows EDC's obtained along the Γ-S symmetry direction in the second BZ. Moving away from the second BZ center at 2.30 Å^{-1} towards the BZ boundary at S, we obtain the spectrum at 2.1 Å^{-1} (dotted curve), and observe a peak crossing the Fermi energy at $k_\parallel=2.04$ Å^{-1} (solid curve). At $k_\parallel=1.98$ Å^{-1} (dashed curve) the intensity at E_F decreases significantly, but increases again dramatically as another peak crosses E_F at 1.92 Å^{-1} (upper solid curve). This is evidence of two bands crossing E_F within an interval of 0.12 Å^{-1} of each other. The next spectrum in the sequence, at 1.86 Å^{-1} (dot-dashed curve), shows a large decrease of the density of states near the Fermi energy, indicating that a band has indeed crossed E_F. The same band crossings are observed in the first BZ. Here we present the results in the second BZ in order to show the expected periodic behavior. In the vicinity of the corner S of the first BZ, at 1.15 Å^{-1}, we find another band dispersing towards E_F, and crossing it at 1.26 Å^{-1} (upper solid line, Fig. 3). If the BZ boundary is approached from the first zone, a mirror image of the behavior in the second zone is observed, with a band crossing E_F at 1.08 Å^{-1} (lower solid line in Fig. 3). It can be seen from the previous figures that as the bands cross E_F there is a large increase in the density of states just below E_F. This may be due to the effect of opening a superconducting gap,[13] although the resolution of 100 meV in our experiments does not allow us to directly

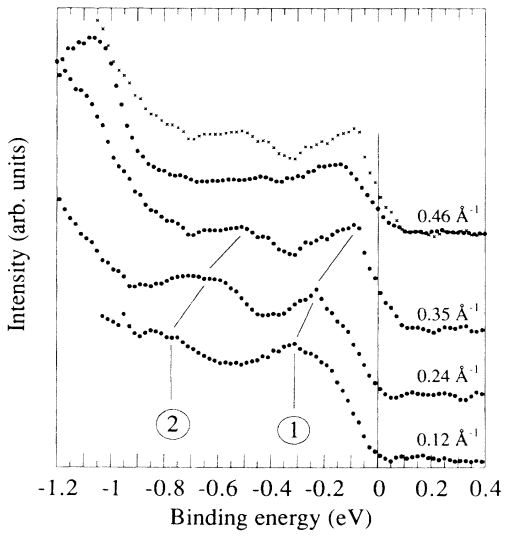

FIG. 1. Energy distribution curves along the Γ-X,Y symmetry direction at (0,0.12), (0,0.24), (0,0.35), and (0,0.46) Å^{-1}. A band can be seen crossing the Fermi energy at (0,0.35) Å^{-1}. The EDC for (0,0.35) Å^{-1} is reproduced as crosses on top of the EDC obtained at (0,0.46) Å^{-1}, showing that a band observed at (0,0.46) Å^{-1} is well below E_F.

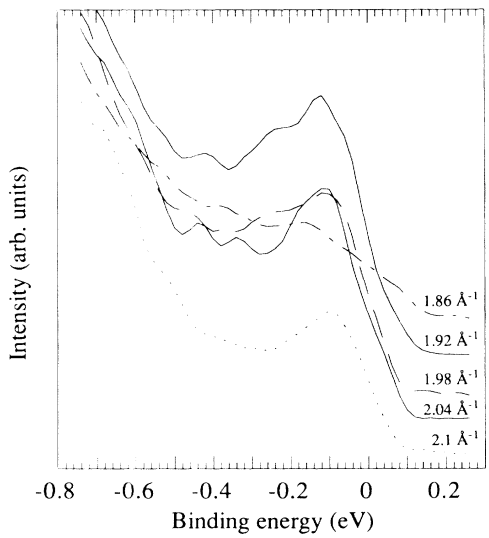

FIG. 2. Energy distribution curves obtained along the Γ-S symmetry direction in the second Brillouin zone obtained at intervals of 0.06 Å^{-1}. Bands cross the Fermi energy at 1.92 and 2.04 Å^{-1} away from Γ. Moving away from Γ in the second BZ, after the second band has crossed E_F the density of states near E_F is greatly reduced (dash-dotted curve).

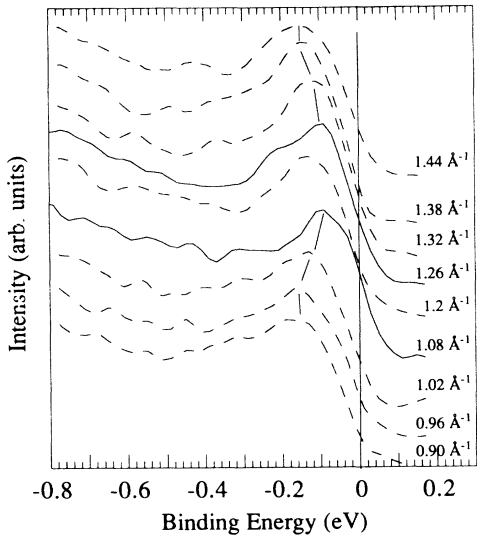

FIG. 3. Energy distribution curves obtained along the Γ-S symmetry direction in the vicinity of the first Brillouin zone boundary (at 1.15 Å^{-1}), at the indicated distances from the zone center. A band crosses the Fermi energy at 1.08 Å^{-1} in the first zone and at 1.26 Å^{-1} in the second zone. The dispersion of the band is also indicated.

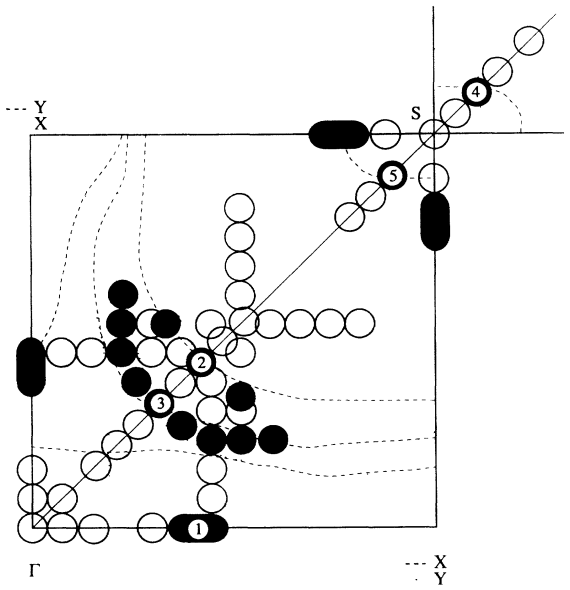

FIG. 4. Experimentally determined Fermi surfaces of $YBa_2Cu_3O_{6.9}$. Filled circles indicate points at which bands cross the Fermi level. The sizes of the circles represent the experimental uncertainty in momentum. The open circles are points in the Brillouin zone at which we did not detect bands crossing E_F. The dashed lines are the Fermi surfaces predicted by Yu *et al.* (Ref. 6). The Fermi-level crossing at the point labeled 1 is shown in Fig. 1, the crossings at points 2 and 3 are shown in Fig. 2, and the crossings at points 4 and 5 are shown in Fig. 3.

resolve the superconducting gap. The locus of all band crossings determines the Fermi surfaces of $YBa_2Cu_3O_{6.9}$, shown in Fig. 4.

The circles in Fig. 4 show the points in the Brillouin zone where we have obtained EDC's. Filled circles indicate points where we detect bands crossing the Fermi level, and open circles indicate no Fermi-level crossings. The size of the circles indicates the precision with which we can identify the band-crossing position in our experiment. The dashed lines are the calculations of Yu *et al.*[6] and the dotted lines show the additional portions of Fermi surface obtained by reflection in the Γ-S direction. Yu *et al.* have argued that as their calculation is for $x=7$, in a rigid-band model with $x=6.9$ the Fermi level would be shifted upwards slightly, such that the heavy bands might no longer cross it. We find that a band does cross the Fermi level along the Γ-X,Y symmetry direction. It is labeled 1 in Fig. 4, and is the crossing shown in Fig. 1 at (0,0.35) Å^{-1}. Its density of states is the highest of all the bands crossing the Fermi level. It is part of a Y-centered hole Fermi surface. The points labeled 2 and 3 are the band crossings equivalent to the ones in the second BZ shown in Fig. 2, at 1.92 and 2.04 Å^{-1}, respectively, and are part of an S-centered hole Fermi surface. The hole pocket around S is also observed at the points marked 4 and 5, shown in Fig. 3, at 1.26 and 1.08 Å^{-1}, respectively.

We do not see any evidence for the chain bands parallel to the Γ-X direction. This result is not too disturbing because one-dimensional states are fragile and easily disrupted by vacancies. At $x=6.9$ a vacancy every twenty atoms is expected, severely disrupting the chain bands. But, in general, there is remarkable agreement between our measurements and the theoretical predictions of Yu *et al.*[6] All of the other predicted Fermi surfaces are observed, including the split bands due to the two CuO_2 planes. There is also good agreement between the Fermi surfaces measured in this experiment and those obtained by means of a positron-annihilation experiment by Smedskjaer *et al.*[14] The positron-annihilation experiments confirm the reason why the photoemission experiments work so well: An a-axis projection shows that the Fermi surfaces have very little k_z dependence. These electronic structures are remarkably two dimensional, as seen in the calculations of Massida, Yu, and Freeman,[5] where the bands in the Z-centered zone are almost identical to those in the Γ-centered zone.

These results show that the S-centered Fermi surfaces in $YBa_2Cu_3O_{6.9}$ enclose a large volume of holes in agreement with the LDA calculations, consistent with the Luttinger theorem. We believe that Fermi surfaces are a general property of high-temperature superconductors. We obtain the same results for $ErBa_2Cu_3O_{6.9}$, (as for $YBa_2Cu_3O_{6.9}$), and other workers[13,15] have shown Fermi-level crossings for $Bi_2CaSr_2Cu_2O_8$ that also agree with LDA calculations. However, this does not imply that excited-state properties of the system, such as band

masses or Fermi velocities, are also accurately predicted by LDA, since by definition, any frequency-dependent self-energy effect (such as the electron-phonon interaction) which would lead to renormalized band masses or Fermi velocities are not included in the calculation. Nonetheless, it appears that a proper theory of the normal-state electronic structure of the high-temperature superconductors should exhibit the same Fermi surfaces as that predicted by LDA calculations.

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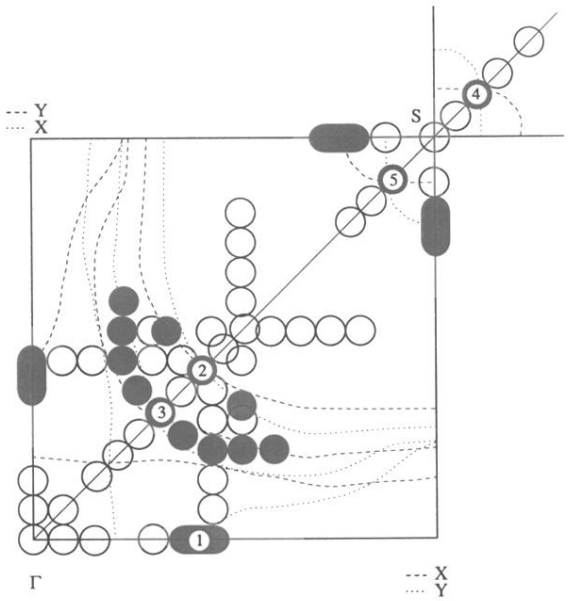

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