Occupied electronic structure and Fermi surface of $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$

G. Mante, R. Claessen, A. Huss, R. Manzke, and M. Skibowski

Institut für Experimentalphysik, Universität Kiel, D-2300 Kiel, Federal Republic of Germany

Th. Wolf, M. Knupfer, and J. Fink

*Kernforschungszentrum Karlsruhe, Institut für Nukleare Festkörperphysik,
P.O. Box 3640, D-7500 Karlsruhe, Federal Republic of Germany*

(Received 25 March 1991)

We have determined the occupied electronic structure and Fermi surface of twinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ single crystals near the Fermi level along the high-symmetry directions of the Brillouin zone at temperatures below 20 K by angle-resolved photoemission spectroscopy of high angular and energy resolution. We observe pronounced structures dispersing from about 0.25 eV at the Γ point upward to the Fermi level, which they cross along Γ -X, Y and Γ -S. Comparison to a recent high-precision local-density-functional band-structure calculation yields only partial agreement. In particular, for several of the theoretically predicted bands we find no experimental evidence, which may in part be explained by the finite oxygen deficiency of our samples. Although the measurements are performed at temperatures well below T_c , we find no indication for the superconductivity energy gap, but are able to identify Fermi-Dirac cutoffs in the spectra within an accuracy of 10 meV. This observation is interpreted as the suppression of superconductivity at the surface and is discussed in relation to the recent discovery of an electronic surface state on $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$.

I. INTRODUCTION

A detailed knowledge of the electronic structure near the Fermi energy of the cuprate superconductors is an essential prerequisite for the understanding of the phenomenon of high- T_c superconductivity. In particular, the question has been posed as to whether the normal-state electronic structure can be described in a Fermi-liquid picture or whether strong correlations among the electrons require a Hubbard-type description^{1,2} or even lead to a ground state as in the so-called Luttinger-liquid model.³ On the experimental side, angle-resolved photoemission spectroscopy (ARPES) is best suited to study such problems, because it directly measures the single-particle excitation spectrum, which in turn is proportional to the imaginary part of the momentum- ($\mathbf{k}$ -) and energy-dependent single-particle Green's function of the system under consideration. Thus ARPES provides detailed information on the $\mathbf{k}$ dependence of the electronic structure (i.e., on band dispersions in the case of a one-electron picture), on self-energy corrections in a more interacting Fermi liquid, and on the existence and topology of the Fermi surface.

A considerable amount of such work has been performed on the system $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$,⁴⁻¹² because the surfaces prepared from single crystals of this compound proved chemically rather inert, which is an indispensable requirement considering the extreme surface sensitivity of ARPES. However, the existence of metallic⁹ and even superconducting (below T_c) Bi-O layers^{12,13} additional to the Cu-O planes common to all cuprate superconductors makes $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ appear somewhat extraordinary among the high- T_c materials. A more typical system for

such studies is therefore the 1:2:3 compound $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$. Unfortunately, ARPES experiments on this material are complicated because of the difficulty of preparing chemically stable surfaces of 1:2:3 compounds under ultrahigh-vacuum conditions at room temperature, because loss of oxygen turns the surface region from a metallic into an insulating state.¹⁴ However, it could be shown that this surface degradation can be suppressed by cleaving the crystals and keeping the surfaces at temperatures below 20 K.¹⁴ Because of these problems and the enormous experimental and preparation efforts required to overcome them, so far only a few experimental studies have been performed on the momentum-resolved electronic structure of $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$, notably on the Fermi surface,¹⁵ the unoccupied electronic structure,¹⁶ and surface states.¹⁷

In this paper we present a high-resolution ARPES study of $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ twinned single crystals with particular focus on the detailed $\mathbf{k}$ dependence of the electronic structure near the Fermi energy along the major high-symmetry directions of the Brillouin zone. The experimental results will be discussed in comparison to the recent high-precision local-density band-structure and Fermi-surface calculation of Pickett, Cohen, and Krakauer.¹⁸

II. EXPERIMENTAL DETAILS

The $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ single crystals were grown using a CuO-BaO self-flux.¹⁹ An Al_2O_3 crucible was used. A mixture of 4 at.% Y_2O_3 , 30 at.% BaCO_3 , and 66 at.% CuO was melted at 1022 °C for 70 h. Crystal growth occurred during slow cooling at a rate of 0.1 °C/h down to

960°C. At the end of the growth process, the melt was decanted into a porcelain capsule placed inside the furnace. Then the furnace was cooled down to room temperature during 144 h. Additional O loading was carried out in pure O atmosphere at 1 bar at various temperatures and times between 620 and 430°C during 100 and 30 h, respectively. The single crystals typically contain <1 at.% Al impurities predominantly on the Cu(1) position. Sharp transition temperatures ($\Delta T = 1.5$ K) between 88.5 to 89.5 K were measured inductively. The linear relationship between oxygen content and the *c*-axis lattice constant was used to determine an oxygen deficiency of $\delta \approx 0.2$. The dimensions of the twinned crystals were about $3 \times 3 \times 1$ mm³.

The ARPES data were taken with HeI radiation ($h\nu = 21.22$ eV) from a rare-gas discharge lamp. Photoelectrons were detected with a hemispherical analyzer mounted on a goniometer, which is independently movable around two axes. The analyzer operated with an energy resolution of 60 meV, and its angular acceptance is proved to be better than $\pm 0.5^\circ$.²⁰ X-ray diffraction and the symmetry of the ARPES spectra for electron takeoff angles around normal emission were utilized for the alignment of the samples, resulting in an overall accuracy of $\pm 1^\circ$. The Fermi edge of a gold film, which was evaporated *in situ* onto the sample holder prior to cleavage of the sample, was used as an energy reference.

The samples were attached to the cold finger of a cryostat by a conducting epoxy glue. The vacuum chamber was baked out moderately for about 20 h with the sample temperature never exceeding 100°C, resulting in a working pressure in the low 10^{-10} mbar range. In addition, a refrigerator-cooled cryopump was used to reduce water and other rest gas contaminants with high sticking coefficients at low temperatures. After cooling down the sample to less than 20 K, *in situ* cleavage was obtained by tearing off an Al lever glued on top of the sample. ARPES was carried out at the same low temperature of less than 20 K in order to avoid oxygen loss from the surface.^{14,21} The quality of the surfaces was controlled by the absence of the notorious 9 eV peak, which is believed to be related to the oxygen depletion of the near-surface region^{14,21} and which became distinctly observable only after heating the samples to above 100 K. At about 16–20 h after cleavage, additional peaks at binding energies of 10.0, 11.2, and 13.6 eV appeared in the spectra, which we attribute to common adsorbates like water and CO. Great care has been taken to avoid this contamination, and only spectra of clean surfaces have been evaluated in this study.

In a previous publication¹⁷ we have reported on the existence of a surface state at about 0.9 eV binding energy near the *X*, *Y* point of the Brillouin zone, which emphasizes the importance of three-dimensional covalent bonds in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as opposed to the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$. The observation of the surface state represents a further criterion for the cleanliness of the surface. However, even when the surface state was completely suppressed as a result of surface contamination, all ARPES structures discussed in this paper remained present, though slightly reduced in intensity. Thus they

can clearly be taken as representative for the bulk electronic structure.

The ARPES measurements were performed along the high-symmetry directions of the Brillouin zone. Because the single crystals are twinned, we cannot distinguish between the Γ -*X* and Γ -*Y* directions, but will measure some average of both high-symmetry lines. Therefore, we will refer to the measured direction as Γ -*X*, *Y*. The Γ -*S* line is unaffected by the twinned character of the samples. Data have been taken on nine different samples with a remarkable reproducibility of the spectra. In particular, the surface peak at the *X*, *Y* point was observed on all freshly cleaved surfaces.

III. RESULTS AND DISCUSSION

In Fig. 1 we show angle-resolved photoemission spectra taken along the Γ -*X*, *Y* direction for electron emission angles from $\vartheta = -12^\circ$ to 54° , corresponding to

FIG. 1. Angle-resolved photoemission spectra of twinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ single crystals measured along the Γ -*X*, *Y* azimuth for varying angles of electron emission corresponding to the first and second Brillouin zone. Cleavage and measurements have been performed at temperatures below 20 K. Peak *S* has been identified as a surface state (Ref. 17).

wave-vector components parallel to the surface ($k_{\parallel}$) in the first and second Brillouin zone (BZ). The zone boundary at the X, Y point is crossed for $\vartheta = 23^\circ$ until for $\vartheta = 50^\circ$ the Γ point in the second BZ (Γ_2) is reached. The spectra around normal emission (i.e., around Γ_1) display a distinct structure at a binding energy of about 1.2 eV, which for increasing positive and negative angles reduces in intensity, until it has merged into a steplike feature at $\vartheta = \pm 12^\circ$. Around the X, Y point an extremely sharp peak ($\Delta E = 100$ meV) is observed at a binding energy of about 0.9 eV, which is denoted by S in Fig. 1. This peak could be identified as a surface-derived electronic state by its strong sensitivity to adsorbates and by its lack of dispersion perpendicular to the surface.¹⁷

In the immediate vicinity of the Fermi energy, distinct structures are only observed for $\vartheta > 30^\circ$, i.e., for $k_{\parallel}$ in the second BZ, while the intensity modulations of the spectra measured in the first BZ are much weaker. This can be seen very clearly from Fig. 2, which shows an enlarged portion of the spectra of Fig. 1 near E_F . The left panel of Fig. 2 contains spectra taken around normal emission in the first BZ. While for $\vartheta = 0^\circ$ hardly any modulation can be identified, we find for increasing angles a structure developing at about 0.2 eV and moving toward E_F , until at

$\vartheta = \pm 12^\circ$ the emission onset becomes rather sharp and resembles a Fermi edge. This behavior is symmetric about $\vartheta = 0^\circ$ and indicates a band dispersing through the Fermi level. Though this structure is reproducible, the low counting statistics due to the small intensities measured in the first BZ does not allow a more detailed analysis.

In contrast, we observed higher count rates and much more pronounced structure for the spectra measured in the second BZ, which are displayed in the right panel of Fig. 2. When following the spectra from low to high emission angles, we find a remarkably sharp onset of emission at the Fermi energy for $\vartheta = 32^\circ$, which at 34° has developed into a distinct asymmetric peak. For even higher angles it becomes broader and disperses away from E_F (marked by the thick tick marks in Fig. 2), until at about 50° (corresponding to Γ_2) it merges into the broad structureless background intensity, which is present in all our spectra. Thus the peak starts out as a rather broad feature centered at about 0.25 eV binding energy near the Γ point (Γ_2) and disperses upwards in energy when going toward X, Y until at $\vartheta = 32^\circ$ it appears to intersect the Fermi level, which is exactly the same behavior as observed for the weak feature in the first BZ. In the inset at the top of the left panel of Fig. 2, we show the $\vartheta = 32^\circ$ spectrum superimposed to the Fermi edge of an *in situ* evaporated gold film measured under identical conditions. The close similarity of both spectra suggests that the emission onset of the $\vartheta = 32^\circ$ spectrum is indeed given by a cutoff due to the Fermi-Dirac distribution function. The implications of the observation of a Fermi edge at temperatures well above T_c will be discussed further below.

However, even when the dispersive peak along $\Gamma-X, Y$ has disappeared for $\vartheta < 32^\circ$, the intensity near E_F does not vanish, but a dispersionless feature seems to remain, whose weak intensity makes it difficult to assign a definite energy position to it. In particular, it is hard to decide whether or not there is another Fermi level crossing near the X, Y point as suggested by the spectra along the $X, Y-S$ line (see below). Similarly, also the spectra at $\vartheta \geq 46^\circ$ display a weak nondispersing structure at about 0.1 eV binding energy (the weak features are marked by thin tick marks in Fig. 2).

ARPES data taken along the $\Gamma-S$ direction are shown in the left panel of Fig. 3. The spectra were measured in the first BZ from normal emission to $\vartheta = 33^\circ$, which corresponds to the S point. As in the $\Gamma-X, Y$ series the spectra around normal emission are rather structureless. At $\vartheta = 7^\circ$ a broad peak appears at about 0.2 eV, which becomes sharper and more pronounced and moves toward E_F as the emission angle increases. Note that the spectra in this region of k space have been taken in steps of 1° . The peak is most pronounced for $\vartheta = 12^\circ$, while already at 13° it has lost most of its intensity. This demonstrates the importance of the high angular resolution used in this study. The disappearance of the peak for $\vartheta > 13^\circ$ indicates a Fermi-level crossing. A comparison of the $\vartheta = 13^\circ$ spectrum with the Fermi edge of gold is shown in the upper right panel of Fig. 3. The spectra at and near the S point ($\vartheta = 33^\circ$) show no distinct structure or indication

FIG. 2. Angle-resolved photoemission spectra of Fig. 1 on an enlarged energy scale measured in the first (left panel) and second (right panel) Brillouin zone. The inset at the top of the left panel shows the $\vartheta = 32^\circ$ spectrum compared to the Fermi edge of an *in situ* evaporated gold film measured under identical conditions.

for a Fermi-Dirac cutoff. Thus, from our data, we have no evidence for the small hole pocket around S , which is expected from band-structure calculations for the ideal compound ($\delta=0$) (Ref. 18) and whose observation with ARPES has been reported by Campuzano *et al.*¹⁵ for $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ (i.e., $\delta \approx 0.1$). As along Γ - X,Y , the Γ - S spectra also exhibit additional small dispersionless features near E_F (thin tick marks in Fig. 3), which, because of their weak appearance, cannot be analyzed in detail.

The lower panel on the right-hand side of Fig. 3 contains the spectra measured along the X,Y - S line. Here we also observe that the intensities of the spectra measured on the X,Y - S edge of the *first* BZ were considerably weaker than those on the edge of the *second* BZ (positions a through c in the drawing of the BZ in Fig. 3). While away from the X,Y point the spectra display no distinct structure, the sharp emission onset at or near

(position a in Fig. 3) X,Y seems to indicate the existence of yet another Fermi edge, though the peak observed in the X,Y spectrum is not as pronounced as the dispersive peaks found along the other high-symmetry directions. The weaker emission onset of the $\vartheta=24^\circ$ spectrum (i.e., at X,Y) of the Γ - X,Y series of Fig. 2 does neither clearly support nor contradict the identification of a Fermi edge in the near- X,Y spectra of Fig. 3, but may simply reflect the general tendency of lower intensities in the first BZ.

We now turn to the discussion of the data. First, we like to comment on the observation that for two of the measured high-symmetry lines (Γ - X,Y and X,Y - S) we found pronounced ARPES structures only in the second BZ, while along Γ - S distinct peaks were observed already in the first BZ. This behavior of the ARPES intensity seems to be just opposite to the results of Campuzano *et al.*,¹⁵ who find pronounced structure along Γ - X,Y in the first BZ, while their Γ - S data appear to be stronger modulated in the second BZ (see Figs. 2 and 3 of Ref. 15). Because in their work a considerably larger photon energy of 50 eV was used (as opposed to the 21.22 eV in our experiment), different final states are involved in both ARPES studies. This in turn results in different matrix elements describing the optical transition, while the alternating behavior of the intensity in the first and second BZ's may reflect some symmetry property of the wave functions of the initial states. It is interesting to note that a recent ARPES experiment on $(\text{Bi}_{1-x}\text{Pb}_x)_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ also found valence-band structures in the second BZ much stronger pronounced than in the first BZ.¹⁰

As discussed above, we observe for all high-symmetry lines peaks dispersing through the Fermi level. In particular, the emission onsets at the $k_{\parallel}$ value of intersection could be identified as due to a Fermi-Dirac cutoff. This is a remarkable observation, because the temperature during this measurement was well below T_c , so that we should expect the samples to be in the superconducting state and observe the superconductivity energy gap. So far, there has been no report of the observation of the gap in $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ by photoemission, which is in striking contrast to the several times reproduced measurements of the gap in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.⁵⁻⁷ From our experimental accuracy we estimate that, if there is a gap at all, it must be smaller than about 10 meV. This result has been confirmed very recently by another high-resolution ARPES study.²² From this negative result and the extreme surface sensitivity of ARPES, we conclude that superconductivity is suppressed on the surface. Recent band-structure calculations¹⁸ suggest that the system $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ possesses a substantial degree of three-dimensional bonding despite of its overall two-dimensional character. Thus the creation of a surface inevitably requires the breaking of strong ionic or covalent bonds, in contrast to the case of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, where cleavage occurs between only weakly van der Waals-bonded Bi-O layers. As a consequence, the cleavage surface has to react in some way to this perturbation and will redistribute the electronic charge at the surface in order to minimize its energy. This example reflected in the occurrence of the surface state near the X,Y point.¹⁷ It should be envisaged that the rearrange-

FIG. 3. Series of angle-resolved photoemission spectra measured in the Γ - S direction (left panel). The upper right panel contains a comparison between the $\vartheta=13^\circ$ spectrum along Γ - S and the Fermi edge of the gold reference. The lower panel on the right shows spectra measured on the X,Y - S line of the second Brillouin zone. The position of these spectra in k space are visualized in the inset and labeled by a , b , and c .

ment of the electronic surface charge may also suffice to suppress surface superconductivity, for example, by possibly affecting the as-yet unknown mediating pairing mechanism.

This interpretation of the nonobservation of the gap by ARPES is not necessarily in contradiction with the gap data obtained by tunneling spectroscopy (see, e.g., Ref. 23), which is likewise surface sensitive.²³ The tunneling results may not be representative for the *free* surface because of the existence of an insulating oxide layer, which could restore the original surface charge distribution by saturating the broken bonds. However, there has recently been a report on the observation of the gap on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ surfaces by high-resolution electron-energy-loss spectroscopy (HREELS).^{24,25} The authors conclude from theoretical arguments and the nonobservation of bulk phonon modes that their measurement is sensitive to only the topmost metallic layers. They observe a characteristic energy loss of about 60 meV, which is ascribed to the superconducting energy gap. There seems to be a problem with this interpretation, because the loss feature remains present even *above* T_c without much change in energy, though it is clearly reduced in intensity. The authors take this as indication for the preexistence of bound electron pairs above T_c and suggest that the transition into the superconducting state be a Bose-Einstein condensation of these pairs.²⁵ Presently, we cannot resolve the apparent disagreement of ARPES and HREELS results on the gap.

Another interesting observation concerns the line shapes of the dispersive ARPES structures. The peaks observed along $\Gamma-X, Y$ and $\Gamma-S$ display a rather asymmetric profile with a tail on the high-binding-energy side. This is not only true for peak positions close to E_F , where the asymmetry could be easily explained by the Fermi-Dirac cutoff, but also away from the Fermi level. Similar line shapes have been observed also for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.^{9,11} Most interestingly, these line shapes are reminiscent of the ARPES profiles expected in the so-called marginal Fermi liquid²⁶ or as calculated by Kampf and Schrieffer for an antiferromagnetically correlated metal.²⁷ In both models the ARPES peaks near the Fermi energy contain only little quasiparticle weight, but are dominated by incoherent intensity reflecting the many-body character of the excitation. We also note that the experimental peaks sit on the edge of a rather unmodulated background intensity, which is visible in all our spectra and is also present in the ARPES spectra of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$.^{9,11} It is not clear, whether it contains several quasiparticle peaks, which lie too close to be resolved, or whether it represents some incoherent intensity. We have not evaluated the photohole-lifetime widths as this was done for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ by Olson *et al.*,¹¹ because the remaining weak structure near the Fermi level (marked by thin bars in Figs. 2 and 3) made it rather difficult to clearly define a width. Furthermore, especially for the dispersive peak along $\Gamma-S$, even our very good k resolution seems not sufficient to rule out broadening effects due to a finite $\Delta k_{\parallel}$. Thus we cannot decide here on a linear-versus-quadratic dependence of the widths on the binding energy,¹¹ but it is obvious from

the spectra in Fig. 2 and 3 that the appearance of the peaks varies from almost indiscernible at the Γ point to very sharp as they approach the Fermi level.

IV. COMPARISON TO BAND-STRUCTURE CALCULATION

In this section we compare the experimental data with the recent high-precision local-density-functional (LDF) calculation of the band structure and Fermi surface by Pickett, Cohen, and Krakauer.¹⁸ Though this calculation finds some three-dimensional effects in the band dispersions resulting in slight but important differences between basal ($\Gamma-X, Y-S$) and top ($Z-U, T-R$) plane of the BZ, we show in Fig. 4 for reasons of clearness only the bands along the basal high-symmetry directions $\Gamma-X, Y$ and $\Gamma-S$. However, it should be noted here that the component of the wave vector perpendicular to the surface ($k_{\perp}$) is not conserved in the photoemission process and is, in principle, indetermined in the ARPES measurements. Our focus will be on the bands, which are close to or even intersect the Fermi energy. In Fig. 4 bands which are located in the Cu-O chains or in the Cu-O₂ planes are denoted by *c* and *p*, respectively. We have converted the ARPES peak positions into experimental $E(k_{\parallel})$ data, which are given by the circles in Fig. 4. Solid circles denote the strongly pronounced ARPES structures.

From our data along $\Gamma-X, Y$ in the second BZ, we find the ARPES feature located at about 0.25 eV near Γ_2 to be in fairly good agreement with theory. In particular, as we move along the $\Gamma-X, Y$ azimuth, this peak seems to follow quite closely the theoretical chain-derived band along $\Gamma-Y$ (i.e., parallel to the Cu-O chains), which in the calculation touches E_F at about $\frac{2}{3}$ the distance from Γ to Y and disperses downward again. In the experiment, however, the peak is observed to cross the Fermi

FIG. 4. Comparison of the ARPES results with the local-density-functional band-structure calculation of Pickett, Cohen, and Krakauer (Ref. 18). Solid and dashed lines in the right panel represent bands in the $\Gamma-Y$ and $\Gamma-X$ directions, respectively. Theoretical bands located in the Cu-O chains and in the Cu-O₂ planes are denoted by *c* and *p*, respectively. The experimental results are marked by circles; solid circles denote pronounced ARPES peaks.

level, which rather resembles the theoretical behavior of this band in the top plane of the BZ, i.e., along the $Z-T$ line (not shown here). In LDF theory the counterpart of this band along the $\Gamma-X$ direction (i.e., perpendicular to the chains) remains below E_F for all values of $k_{\parallel}$, which could account for the weak structure at 0.1 eV in the spectra of Fig. 2 taken for $\vartheta=24^{\circ}-30^{\circ}$. Remember that, because of the twinning of the crystals, we average over both directions. The LDF calculation also predicts a strongly dispersive chain-derived band along $\Gamma-Y$, which intersects the Fermi level at about $\frac{1}{4}$ the distance from Γ to Y and which has no counterpart along $\Gamma-X$, reflecting its one-dimensional character. It is surprising that apart from the weak obviously nondispersive feature at about 0.1 eV around the Γ_2 point (see Fig. 2), we have no experimental indication for this band or even its strong dispersion. In their ARPES study Campuzano *et al.*¹⁵ observe a band along $\Gamma-X, Y$ dispersing from 0.3 eV at Γ upward to the Fermi energy at $k_{\parallel}=0.35 \text{ \AA}^{-1}$. This value of the Fermi vector (k_F) is about halfway between the theoretical crossing point of the strongly dispersive chain band and the k_F we observed for the flat chain-derived band. It is not clear which band their observation of a Fermi edge along $\Gamma-X, Y$ has to be ascribed to when compared to the calculation of Pickett, Cohen, and Krakauer.¹⁸ Thus there seems to be no unambiguous experimental indication by ARPES for the strongly dispersive one-dimensional chain band so far.

Along the $\Gamma-S$ direction the LDF calculation predicts three bands to disperse through the Fermi level at about $\frac{1}{3}$ of the BZ extension, one chain-derived band and two located in the Cu-O_2 plane. In the $\Gamma-S$ spectra (cf. Fig. 3) only one peak can be resolved, which crosses E_F at a slightly larger $k_{\parallel}$. The slope of the experimental dispersion seems to be somewhat smaller than expected in the theory. The occupied bandwidth derived from the ARPES data is about 0.25 eV, in agreement with the theoretical values for the chain band and one of the plane bands, but there is no experimental evidence for the theoretical 0.5-eV occupied bandwidth of the other plane band, whose calculated Fermi vector, on the other hand, is closest to the experimental one. Also, we have no experimental indication for the theoretical chain-derived band which intersects the Fermi level near the S point, in contrast to its observation by Campuzano *et al.*¹⁵

It should be noted here that the LDF calculation of Pickett, Cohen, and Krakauer¹⁸ is performed for the ideal stoichiometric compound $\text{YBa}_2\text{Cu}_3\text{O}_7$, while our measurements have been made on oxygen-deficient samples with $\delta \approx 0.2$, which is to be expected to affect the electronic structure substantially, especially the chain-derived bands (because the oxygen vacancies reside in the Cu-O chains). One could assume that missing oxygen simply results in a reduction of holes and a subsequent upward shift of the Fermi energy. However, as Pickett, Cohen, and Krakauer remark in their paper,¹⁸ changes in the band structure are not likely to follow a rigid-band picture, because the absence of an oxygen atom changes the local potential drastically as well as the electron count. The change in potential may well introduce local

distortions as well, which will give additional non-rigid-band behavior. We believe that the difference in oxygen deficiency also accounts for the discrepancies between our study of $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ ($\delta \approx 0.2$) and that of Campuzano *et al.*¹⁵ on $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ ($\delta \approx 0.1$).

We already mentioned before that the ARPES spectra also exhibit a structureless background at binding energies above ≈ 0.2 eV. In this energy range the theoretical band structure shows a wealth of bands (see Fig. 4). It is presently an open question as to whether the finite-energy resolution and intrinsic broadening of these bands does not allow to resolve them or whether the background reflects properties of the electronic structure, which cannot be accounted for in a one-electron picture, as discussed above.

Figure 5 shows the Fermi surface for all values of $k_{\perp}$ projected onto the basal ($k_{\perp}=0$) plane of the BZ as calculated in Ref. 18. The circles denote positions in k space, where ARPES spectra were measured. Observations of Fermi-Dirac cutoffs are marked by solid symbols. As seen from the figure and already discussed above, we find only partial agreement with theory. In particular, we do not observe the small hole pocket around S (R) and are not able to resolve all theoretically expected Fermi edges along $\Gamma-S$. From the experimentally determined position of the Fermi vector along $\Gamma-S$, the large hole surfaces appear to be somewhat shrunk in comparison to theory, which together with the absence of the small hole pocket at S could be well understood in a rigid-band picture (despite the remark of Pickett, Cohen, and Krakauer quoted above). A rigid shift of the band structure to lower energies (i.e., an upward shift of the Fermi energy) due to a finite oxygen deficiency would

FIG. 5. Projection of the theoretical Fermi surface of Ref. 18 onto the basal ($k_{\perp}=0$) plane of the Brillouin zone. The shaded regions indicate values of $k_{\parallel}$, for which there is a Fermi surface for some value of $k_{\perp}$. Open circles mark points in k space, where ARPES spectra have been measured. Solid circles denote the observation of a Fermi-Dirac cutoff (the circles along the $X, Y-S$ line are only half-filled, because here the observation and localization of a Fermi edge was not as unambiguous as along the other high-symmetry directions).

cause the chain-derived band near S to become completely occupied and the Fermi vectors along $\Gamma-S$ to move toward the S point, which is exactly, what we observe. This would also explain, why we do not see Fermi edges due to the large hole surfaces along $X, Y-S$, because they would appear at wave vectors, where we have not taken spectra. However, this rigid-band picture does not explain the dispersion and Fermi vector observed along the $\Gamma-X, Y$ line

In summary, we find only partial agreement between experimental results and the LDF calculation of Pickett, Cohen, and Krakauer. In particular, the theory predicts bands, for which we found no experimental evidence from our spectra. This can at least in part be attributed to the nonideal oxygen stoichiometry of our samples, though we cannot rule out completely a suppression of photoemission from some of these bands due to matrix element effects. In any case, several aspects of the band picture such as dispersions, existence of a Fermi surface, and position of Fermi vectors seem to be reflected in the ARPES data.

V. SUMMARY

We have measured the electronic structure of twinned $\text{YBa}_2\text{Cu}_3\text{O}_{6.8}$ single crystals near the Fermi energy by high-resolution angle-resolved photoemission spectroscopy. The spectra show pronounced dispersive peaks along the $\Gamma-X, Y$ and $\Gamma-S$ high-symmetry directions, which are observed to cross the Fermi level. The intensities of these peaks differ significantly in the first and second Brillouin zone due to matrix-element effects. The asymmetric line shapes of the ARPES structures are highly unusual and are reminiscent of ARPES line profiles expected from theoretical models of strongly correlated electron systems. A comparison of the data to the recent

local-density-functional band-structure calculation of Pickett, Cohen, and Krakauer¹⁸ yields only partial agreement. While the dispersion of the experimental peaks and the measured occupied bandwidth of 0.25 eV seems to be reasonably reproduced by some of the calculated bands, we find no experimental evidence for the dispersion or even existence of several other theoretical bands. This can at least in part be ascribed to the nonideal oxygen stoichiometry of our samples, which possibly also accounts for the discrepancies to the ARPES study by Campuzano *et al.*¹⁵ on $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$.

From the fact that despite the low temperatures far below T_c we observe Fermi-Dirac cutoffs in the spectra to within an experimental accuracy of 10 meV, we conclude that superconductivity is suppressed at the surface. This is related to a possible electronic redistribution of surface charge caused by the breaking of three-dimensional bonds during cleavage, which is evident from the occurrence of an electronic surface state.

In conclusion, the experimental results on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ contain aspects which may be explained in terms of well-defined quasiparticles in a Fermi-liquid picture. However, we cannot exclude from the present data that structures observed in our ARPES spectra are of partially or completely incoherent nature. Also, progress is needed in the preparation of large single crystals with an oxygen content as close to the ideal stoichiometry as possible, which would allow a more systematic comparison to band-structure calculations.

ACKNOWLEDGMENTS

This work has been supported by the Bundesministerium für Forschung und Technologie under Project No. 05 401 AAI 1.

¹Proceedings of the 2nd International Conference on High Temperature Superconductors and Materials and Mechanism of Superconductivity (Stanford, 1989), edited by W. Harrison, N. Phillips, and R. Shelton, special issue of *Physics C* **162-164** (1989).

²*Proceedings of the International Winter School on the Electronic Properties of High- T_c Superconductors and Related Compounds* (Kirchberg, 1990), Vol. 99 of *Springer Series in Solid-State Physics*, edited by H. Kuzmany, M. Mehring, and J. Fink (Springer, New York, 1990).

³P. W. Anderson, *Phys. Rev. Lett.* **64**, 1839 (1990).

⁴T. Takahashi, H. Matsuyama, H. Katayama-Yoshida, Y. Okabe, S. Hosoya, K. Seki, H. Fujimoto, M. Sato, and H. Inokuchi, *Nature* (London) **334**, 691 (1988).

⁵J.-M. Imer, F. Patthey, B. Dardel, W.-D. Schneider, Y. Baer, Y. Petroff, and A. Zettl, *Phys. Rev. Lett.* **62**, 336 (1989).

⁶C. G. Olson, R. Liu, A.-B. Yang, D. W. Lynch, J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Science* **245**, 731 (1989).

⁷R. Manzke, T. Buslaps, R. Claessen, and J. Fink, *Europhys. Lett.* **9**, 477 (1989).

⁸R. Claessen, R. Manzke, H. Cartensen, B. Burandt, T. Buslaps, M. Skibowski, and J. Fink, *Phys. Rev. B* **39**, 7316 (1989).

⁹G. Mante, R. Claessen, T. Buslaps, S. Harm, R. Manzke, M.

Skibowski, and J. Fink, *Z. Phys. B* **80**, 181 (1990).

¹⁰R. Böttner, N. Schroeder, E. Dietz, U. Gerhardt, W. Assmus, and J. Kowalewski, *Phys. Rev. B* **41**, 8679 (1990).

¹¹C. G. Olson, R. Liu, D. W. Lynch, R. S. List, A. J. Arko, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, *Phys. Rev. B* **42**, 381 (1990).

¹²B. O. Wells, Z.-X. Shen, D. S. Dessau, W. E. Spicer, C. G. Olson, D. B. Mitzi, A. Kapitulnik, R. S. List, and A. Arko, *Phys. Rev. Lett.* **65**, 3056 (1990).

¹³Chen Wang, B. Giambattista, C. G. Slough, R. V. Coleman, and M. A. Subramanian, *Phys. Rev. B* **42**, 8890 (1990).

¹⁴R. S. List, A. J. Arko, Z. Fisk, S.-W. Cheong, S. D. Conradson, J. D. Thompson, B. Pierce, D. E. Peterson, R. J. Bartlett, N. D. Shinn, J. E. Schirber, B. W. Veal, A. P. Paulikas, and J. C. Campuzano, *Phys. Rev. B* **38**, 11 966 (1988).

¹⁵J. C. Campuzano, G. Jennings, M. Faiz, L. Beaulaigue, B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, R. S. List, A. J. Arko, and R. J. Bartlett, *Phys. Rev. Lett.* **64**, 2308 (1990).

¹⁶T. J. Wagener, Y.-H. Hu, M. B. Jost, and J. H. Weaver, *Phys. Rev. B* **42**, 1041 (1990).

¹⁷R. Claessen, G. Mante, A. Huss, R. Manzke, M. Skibowski, Th. Wolf, and J. Fink, *Phys. Rev. B* **44**, 2399 (1991).

¹⁸W. E. Pickett, R. E. Cohen, and H. Krakauer, *Phys. Rev. B*

- 42, 8764 (1990).
- ¹⁹Th. Wolf, W. Goldacker, B. Obst, G. Roth, and R. Flükiger, *J. Cryst. Growth* **96**, 1010 (1989).
- ²⁰O. Anderson, R. Manzke, and M. Skibowski, *Phys. Rev. Lett.* **55**, 2188 (1985).
- ²¹A. J. Arko, R. S. List, R. J. Bartlett, S.-W. Cheong, Z. Fisk, J. D. Thompson, C. G. Olson, A.-B. Yang, R. Liu, C. Gu, B. W. Veal, J. Z. Liu, A. P. Paulikas, K. Vandervoort, H. Claus, J. C. Campuzano, J. E. Schirber, and N. D. Shinn, *Phys. Rev. B* **40**, 2268 (1989).
- ²²J. G. Tobin, C. G. Olson, C. Gu, J. Z. Liu, F. R. Solal, M. J. Fluss, R. H. Howell, J. C. O'Brien, H. B. Radousky, and P. A. Sterne (unpublished).
- ²³M. Gurvitch, J. M. Valles, Jr., A. M. Cucolo, R. C. Dynes, J. P. Garino, L. F. Schneemeyer, and J. V. Waszczak, *Phys. Rev. Lett.* **63**, 1008 (1989).
- ²⁴J. E. Demuth, B. N. J. Persson, F. Holtzberg, and C. V. Chandrasekhar, *Phys. Rev. Lett.* **64**, 603 (1990).
- ²⁵B. N. J. Persson and J. E. Demuth, *Phys. Rev. B* **42**, 8057 (1990).
- ²⁶C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. E. Ruckenstein, *Phys. Rev. Lett.* **63**, 1996 (1989).
- ²⁷A. P. Kampf and J. R. Schrieffer, *Phys. Rev. B* **42**, 7967 (1990).