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Evidence for a surface-derived electronic state on YBa₂Cu₃O_{6.8}

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

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

Th. Wolf and J. Fink

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

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From angle-resolved photoemission spectroscopy performed on cleaved surfaces of twinned YBa₂-Cu₃O_{6.8} single crystals, we found strong evidence for the existence of an intrinsic surface-derived electronic band in this high-temperature superconductor. It is observable only near the X(Y) point of the Brillouin zone, showing slight k_{\parallel} — and almost no k_{\perp} —dispersion and a very pronounced sensitivity to surface contamination. We discuss the relation of this state to possible crystal terminations and compare to a calculation of the surface electronic structure.

Photoemission spectroscopy (PES) has provided valuable experimental information on the electronic structure of high-temperature superconductors (HTSCs) in both their normal and superconducting state.¹ However, since PES is a very surface-sensitive method with a probing depth of about 5-30 Å, depending on the kinetic energy of the photoelectrons, the question of how far the measured surface electronic structure is representative for the bulk properties has to be proposed. For the HTSC compound Bi₂Sr₂CaCu₂O₈ this problem seems to be solved because chemically stable surfaces are prepared by cleavage between adjacent Bi-O layers,² which are coupled only weakly by a van der Waals-like bonding with almost no valence charge between them. Thus, the creation of a surface represents no major disturbance to the volume electronic structure in this material. The situation is rather different for $RBa_2Cu_3O_{7-x}$ (1:2:3 compounds), where R stands for a rare-earth element. In this case, the formation of a surface inevitably requires the breaking of strong ionic or covalent bonds between layers. Since in the bulk there is a charge transfer from the CuO_2 layers to the one-dimensional CuO₃ ribbons, the creation of a surface on any layer should lead to a rearrangement of the electronic charge and thus to a change of the surface electronic structure compared to that of the bulk. This has been confirmed by the band structure calculations of Calandra and co-workers, ^{3,4} who find distinct modifications of the surface-derived density of states (DOS) with respect to the volume. Matters are even further complicated by the difficulty of preparing chemically stable 1:2:3 surfaces under ultrahigh vacuum conditions at room temperature, because loss of oxygen turns the surface region from a metal into an insulator, as reported by List et al.⁵ They also have shown that this problem can be overcome by performing PES experiments at temperatures below 20 K.

In this paper we report on evidence from angle-resolved photoemission spectroscopy (ARPES) on $YBa_2Cu_3O_{6.8}$ for the existence of a surface-derived electronic state in this compound. The implications of this observation for the interpretation of the photoemission results and, in particular, for the determination of the superconducting energy gap by PES is discussed. A fuller account of our ARPES data on the bulk electronic structure near the Fermi level will be given in a separate publication.⁶

The single crystals of $YBa_2Cu_3O_{6.8}$ were grown using a CuO-BaO self flux.⁷ An Al₂O₃ crucible was used. A mixture of 4 at. % Y₂O₃, 30 at. % BaCO₃, 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 contain typically < 1 at. % Al impurities predominantly on the Cu(1) position. Sharp transition temperatures (1.5 K) between 88.5-89.5 K were measured inductively. The dimensions of the twinned crystals were about $3 \times 3 \times 1$ mm³.

The ARPES data were taken with HeI radiation from a rare-gas discharge lamp and synchrotron radiation from the DORISII storage ring at HASYLAB, Hamburg. Photoelectrons were detected with a hemispherical analyzer mounted on a goniometer, which is independently rotatable around two axes. The analyzer operated with an energy resolution of 60 meV, its angular acceptance was smaller than $\pm 0.5^{\circ}$. X-ray diffraction and the symmetry of the ARPES spectra for electron take-off angles around normal emission were utilized for the alignment of the samples, resulting in an overall accuracy of $\pm 1^{\circ}$.

The samples were attached to the cold finger of a cryostat by a conducting epoxy glue. 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 a sample temperature of less than 20 K in order to avoid oxygen loss from the surface. The quality of the surfaces were judged by the observation of Fermi edges of certain angles of electron emission and by the absence of the notorious -9-eV peak, which is related to the oxygen depletion of the surface region⁸ and became clearly observable only after heating up the sam-

<u>44</u> 2399

2400

ples to above 100 K. The measurements were performed on four different samples, and the presented spectra were reproducible for all of them.

Figure 1 shows energy distribution curves (EDCs) for binding energies between 0.5 and 1.5 eV taken along the Γ -X, Y azimuth at emission angles corresponding to inplane wave-vector components k_{\parallel} around the Brillouinzone boundary. Following the spectra from low to high values of k_{\parallel} a peak at a binding energy of 1 eV develops out of a step-like feature acquiring its full strength at the zone boundary (X or Y point). Going to higher k_{\parallel} the peak intensity decreases again until it completely disappears in the EDC taken for $k_{\parallel} = 1.12 \text{ Å}^{-1}$. Evaluating the energy position of the peak maximum yields a minimum binding energy of 0.92 eV at the zone boundary and a dispersion of about 70 meV in the k_{\parallel} range, where it can be observed, being symmetrical about the X(Y) point. What is most remarkable about this feature is its small full width at half maximum (FWHM) of 120 meV, which after correcting for the instrumental resolution yields an intrinsic width of 100 meV. This extraordinary low value is reminiscent of the widths found for surface states in metals; see, e.g., for Cu, Refs. 9 and 10.

Evidence for the surface nature of the 1-eV emission is given by its sensitivity to adsorbates. Because the EDCs were taken at temperatures less than 20 K the sticking coefficient of residual molecules in the vacuum chamber hitting the sample approaches unity, so that after some

time the surface will become contaminated by an adsorbate layer. In Fig. 2 we display several EDCs taken at the X(Y) point as a function of time. Spectrum 1 was recorded 1.5 h after cleavage, showing the 1-eV peak with its full intensity. Already 6 h after cleavage it appears to be strongly reduced (spectrum 2), until it becomes completely suppressed after about 13 h (spectrum 3). The vanishing of the peak coincides with appearance of welldeveloped structures at binding energies of 10, 11.2, and 13.6 eV (not shown here), which can be attributed to common adsorbates such as water and CO. Since the contaminants are only physisorbed on the surface, they can be removed by heating the sample to slightly higher temperatures,⁸ which is monitored by the disappearance of the adsorbate-related peaks. As is seen from spectrum 4 in Fig. 2, which was recorded shortly after spectrum 3, but with the sample having been heated to 50 K for a few minutes, the 1-eV peak can at least partly be recovered, as the contaminants desorb. Its observed shift of about 50 meV to higher binding energy may be due to residual adsorbates. It should be noticed in the EDCs of Fig. 2 that the photoemission intensity near the Fermi energy and the shape of the step-like feature at 1-eV binding energy do not seem to be affected at all. From this observation we may conclude that these features are related to the bulkderived electronic structure and that the surface coverage is in the submonolayer range. The same coverage of sur-





FIG. 1. Angle-resolved photoemission spectra of YBa₂Cu₃-O_{6.8} taken with 21.22-eV photon energy along the Γ -X, Y azimuth in the first and second Brillouin zone at T < 20 K. The dashed line indicates the k_{\parallel} dispersion of the peak at 1-eV binding energy. Note that the energy scale is only 1 eV wide.

FIG. 2. Angle-resolved EDCs (hv = 21.22 eV) at the X (Y) point recorded 1.5, 6, and 13 h after cleavage (spectra 1, 2, and 3, respectively). Spectrum 4 shows the effect of flashing the sample to 50 K for about 5 min; the arrow denotes the reappearance of the 1-eV peak. The spectra are normalized to the intensity at 1.5 eV.

face contaminants, however, obviously suffices to quench the 1-eV peak, which is exactly the behavior expected from a surface-related electronic state.

Further indication for the surface character comes from EDCs taken with different photon energies. Figure 3 shows spectra with the photoelectron emission angle adjusted such that the in-plane component of the wave vector (k_{\parallel}) for the 1-eV peak in all EDCs corresponds to the X(Y) point, while the component perpendicular to the surface (k_{\perp}) varies with photon energy. An exact determination of the values of k_{\perp} would require a knowledge of the inner potential of the crystal, but a rough estimate shows that by the used photon energies of 21.22, 23, and 26 eV at least one-third of the Brillouin-zone extension along the c axis is scanned. Evaluating the peak positions from the EDCs of Fig. 3 gives an almost negligible k_{\perp} dispersion of about 30 meV, showing the strong localization of the state parallel to the c axis as is characteristic for a surface state.

Combining its extraordinarily small FWHM, its distinct sensitivity to surface contamination, and the lack of k_{\perp} dispersion, the 1-eV peak has to be interpreted as a surface-derived electronic state. Despite the wealth of photoemission data published up to now, this is a unique observation of a surface state on a high-temperature superconductor. Because of its reduced lifetime at 20 K due to contaminations and its occurrence in relatively small k_{\parallel} range around the X(Y) point, the 1-eV state may have been easily overlooked in previous PES experiments, even in the thorough ARPES study of Campuzano et al.¹¹ The observation of k_{\parallel} dispersion symmetrical about the zone boundary rules out an assignment to a localized defect state, but suggests an interpretation as an intrinsic surface band, which near the X(Y) point lies in the gap of the projected bulk band structure and merges into the bulk band region away from it. Additionally, we can exclude any relationship of this state to the twinned character of



FIG. 3. Angle-resolved EDCs at the X(Y) point for various photon energies.

the samples, because it has recently been observed also in ARPES measurements of untwinned crystals.¹²

To our knowledge no calculations exist of the momentum-resolved surface electronic structure in the literature to compare with, but Calandra and co-workers^{3,4} have determined the surface DOS for several crystal terminations, finding marked changes in comparison to the bulk DOS. It is clear that the atomic and orbital character of the surface state depends strongly on the actual cleavage plane. As Calandra et al. point out, among the possible crystal terminations the Ba-O(4) surface with a Cu(1)-O(1) sublayer is the only nonpolar one, whose electrostatic neutrality enhances its stability with respect to other basal plane surfaces. For this surface the missing of the CuO_2 -Y-CuO₂ layer complex with a charge of about -1 per formula unit (in an ionic picture) above the BaO layer reduces the hole concentration on the O(4) atoms leading to an O(4) valency closer to -2 and, therefore, to an almost neutral BaO surface layer. Then states of the O(4) atom at E_F should be filled by a lowering in energy. This picture is in agreement with the calculations of Calandra et al.³ which predict a very strong O(4)-derived peak in the surface DOS at -0.8 eV, which is not present in the bulk and can be compared to our experimental value of -0.92 eV at the X (Y) point. In addition, by xray photoemission spectroscopy¹³ and PES in the constant-final-state mode¹⁴ the Ba core levels were found to display shifted components, which are believed to represent a Ba surface species, which also suggests a termination at the Ba-O(4) plane.

From its finite k_{\parallel} dispersion symmetrically about the Brillouin-zone boundary and its existence also on untwinned crystals we believe that the 0.92-eV peak is due to an intrinsic surface state, though we do not have an explicit experimental indication of which surface termination it has to be attributed to, but can speculate on its origin only on theoretical grounds as discussed above. Recent high-resolution electron-energy-loss spectroscopy^{15,16} (HREELS) found strong surface inhomogeneities due to a variety of terminal surfaces. In any case, the observation of a surface state clearly demonstrates that at least one termination reacts to cleavage by a rearrangement of surface charge in order to minimize its energy. Nevertheless, the observation of spectral features, that remain grossly unaffected by adsorbates and which are in partial agreement with bulk band-structure calculations, shows that ARPES is still able to provide information also on the volume properties.^{6,11} It may also be interesting to note, that high-resolution ARPES (Refs. 11 and 12) observed the cleavage surface of YBa₂Cu₃O_{7- δ} to remain metallic to within an accuracy of 10 meV at temperatures far below T_c , as opposed to the case of Bi₂Sr₂CaCu₂O₈, where a superconductivity energy gap of about 20-30 meV could reproducibly be detected.¹⁷ This is in contrast to the HREELS results, which observe low-resistivity superconducting and high-resistivity nonsuperconducting areas on the surfaces of both high-temperature superconductors. 15,16

In summary, from ARPES performed on cleaved surfaces of $YBa_2Cu_3O_{6.8}$ single crystals there is strong evidence for the existence of a surface-derived electronic 2402

R. CLAESSEN et al.

band. The assignment as a surface state becomes possible by the sensitivity to adsorbates and the lack of k_{\perp} dispersion. The symmetrical k_{\parallel} dispersion about the Brillouinzone boundary and its observation also on untwinned crystals suggest an intrinsic nature of this state. We gratefully acknowledge helpful discussion with S. Hüfner and P. Steiner regarding the chemical nature of the surface. This work was supported by the Bundesministerium für Forschung und Technologie under Project No. 05 401 AAI 1.

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