ON THE SURFACE-DERIVED STATE OF CLEAVED YBa$_2$Cu$_3$O$_{7-\delta}$ SINGLE CRYSTALS

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Angle-resolved photoemission experiments on the cleaved surface of YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals revealed an intrinsic surface-derived electronic state around the X and Y point of the Brillouin zone with 0.92 eV binding energy. A surface electronic structure different to the bulk can be of basic importance for the surface superconductivity of this high-T_c cuprate. Here we briefly review recent experimental results and present new hydrogen adsorption experiments, demonstrating the surface character of the 0.92 eV state.

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1. Introduction

Angle-resolved photoemission spectroscopy (ARPES) performed with high energy and momentum resolution on single-crystalline high-T_c superconductor surfaces has provided valuable experimental information on the electronic structure in both their normal and superconducting states. Most of the results concerning the origin of the electronic states, their binding energies and dispersions, the Fermi surface in the normal state, and the opening of the superconducting gap for $T < T_c$ were obtained on the system Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (see e.g. [1]). For YBa$_2$Cu$_3$O$_{7-\delta}$ it is a puzzling problem why no superconducting gap could be detected by ARPES. Arko et al. [2] have shown that the YBa$_2$Cu$_3$O$_{7-\delta}$ surface is not stable in vacuum at room temperature but that the surface remains stable if the sample is cleaved and kept at very low temperatures. Under these conditions a Fermi edge is observed for certain k values, but no superconducting gap has been realized [3–6]. Since ARPES is a very surface sensitive spectroscopic technique with a probing depth of about 5–30 Å, the question has to be posed, how far the electronic structure derived from the surface of superconductors is representative for the bulk properties.

For the high-T_c compound YBa$_2$Cu$_3$O$_{7-\delta}$ the formation of a surface by cleavage inevitably requires breaking of strong ionic or covalent bonds between

the layers. In particular, cleavage between the Ba–O and Cu–O planes obtained by cleavages from the top of the sample, the charge transfer in the bulk from the CuO_3 chains to the CuO_2 planes may lead to a rearrangement of electronic charge and thus to changes of the electronic structure at the surface compared to that of the bulk. Such surface effects have been first proposed by Calandra et al. [7, 8], finding distinct modifications of the surface-derived density of states with respect to the bulk. The present contribution adresses the experimental evidence for surface effects on $YBa_2Cu_3O_{6.8}$, obtained from recent high-resolution angle-resolved photoemission studies [4, 9] and new hydrogen adsorption experiments.

2. Experimental

The preparation of the samples with a sharp transition temperature of 1.5 K between 88.5–89.5 K is described elsewhere [4]. The samples were attached to the cold finger of a cryostat by a conducting glue and were cleaved in ultra-high vacuum (base pressure in the low 10^{-10} mbar range, produced by a refrigerator-cooled cryopump) after they were cooled down to less than 20 K.

The photoemission spectra were taken with HeI radiation ($h\nu = 21.22$ eV) by means of a spherical analyzer mounted on a two-axes goniometer. The energy resolution was 25 meV, the angle resolution better than 0.5°. In order to avoid oxygen loss from the surface the sample temperature was kept below 20 K for all experiments. The quality was judged by the strength of the Fermi edge for certain emission angles, the absence of the notorious 9 eV peak, which is related to oxygen depletion in the surface region [10], and the intensity and sharpness of the surface peak at 0.92 eV binding energy which will be discussed in detail below. Molecular hydrogen of high purity is adsorbed on the surface via an ultra-high vacuum valve from a bakable reservoir.

3. Results and discussion

During systematic ARPES studies of the Fermi surface and of occupied dispersive bulk-derived bands close to E_F of $YBa_2Cu_3O_{6.8}$ we have observed a sharp and intense peak around the $X(Y)$-point of the Brillouin zone [4]. In Fig. 1 typical energy distribution curves for this peak are shown between 0.5 and 1.5 eV taken along the Γ–X, Y direction at emission angles corresponding to wave vectors $k_\parallel$ around the Brillouin zone boundary. Such a spectra series is representative for this material and in agreement with previous [4–6] and very recent [12] data on twinned and untwinned samples from different laboratories. Besides several dispersing emission maxima close to E_F, which have been discussed in detail with respect to the bulk band structure calculated within the local density approximation [4], the pronounced maximum (assigned S) with dispersion parallel to the surface, $k_\parallel$, around the $X(Y)$-point is discussed in detail in Ref. [9]. Its intensity is strongest at the $X(Y)$-point, decreasing dramatically away from $X(Y)$, and vanishing at a distance of about 1/3 of the Brillouin zone extension. Within this regime the $k_\parallel$ dispersion is about 70 meV, shown together with the most prominent bulk band at E_F (for details see Ref. [4]) in Fig. 2. The binding energy of S is 0.92 eV at $X(Y)$.
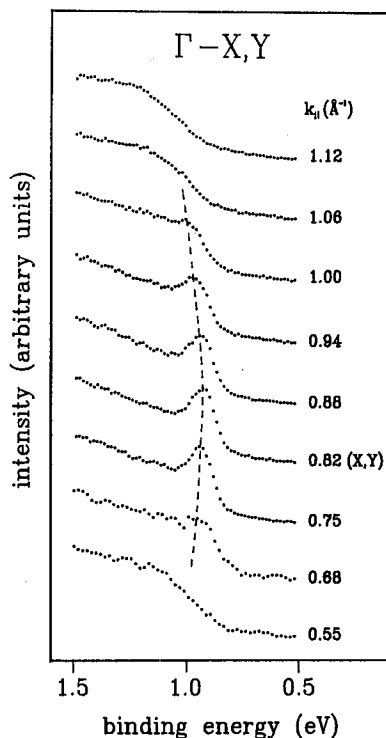
Fig. 1.   Angle resolved photoemission spectra of a $YBa_2Cu_3O_{6.8}$ twinned single crystal taken with 21.22 eV photon energy along the $\Gamma-X,Y$ direction in the first and second Brillouin zone at $T < 20$ K.

The extraordinary low value of the intrinsic linewidth of S of about 100 meV (FWHM) made this peak the one of the sharpest emissions observed in high-T_c materials so far. Such a small band width is reminiscent of widths found for surface states in metals, e.g. Cu metal. Because of these properties and the fact that band S has no direct equivalent in the bulk band structure it is attributed to a surface-derived state [9]. The observation of $k_\parallel$ dispersion rules out an assignment to a localized defect state, but supports an interpretation as an intrinsic surface band, which is located in a gap of the projected bulk band structure near the $X(Y)$-point (due to a surface state) and merges into the bulk band region becoming a surface resonance away from it.

Further evidence for the surface nature of band S is given by the absence of $k_\perp$ dispersion proved by photon energy dependent measurements. Thus, S is localized perpendicular to the c-axis as is characteristic of a surface state. In addition, band S reveals a strong sensitivity to adsorbates. In Ref. [9] we described contamination experiments.

In Fig. 3 we show a spectra series obtained with hydrogen. The spectrum on the bottom is an example for a fresh surface recorded within 20 minutes after
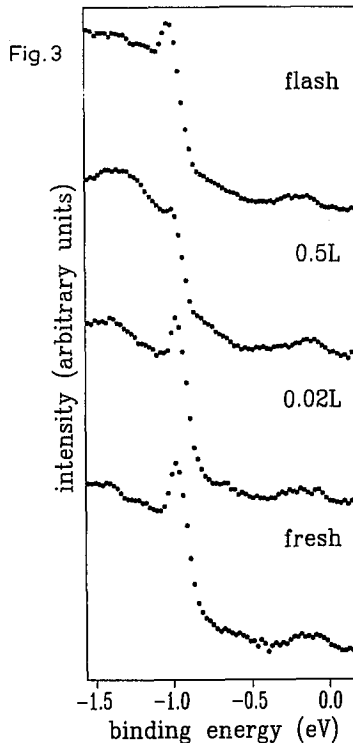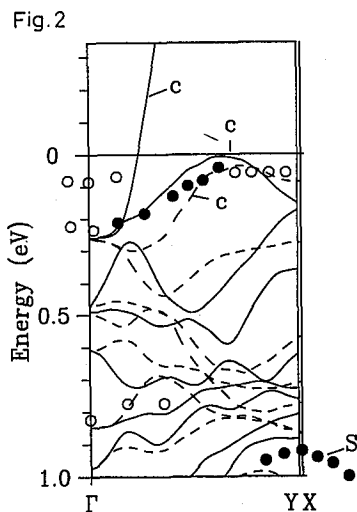
Fig. 2.   Comparison of the ARPES results of $YBa_2Cu_3O_{6.8}$ with a LDA band structure [11]. Solid and dashed lines represent theoretical bands along the Γ-X and Γ-Y direction respectively, and c assigns Cu–O chain bands. Full circles denote pronounced ARPES peaks, open circles — weaker structures and shoulders. Note the $k_{\parallel}$-dispersion of the surface band S from the series of Fig. 1 around the $X(Y)$ point.

Fig. 3.   Sensitivity of the surface band S on hydrogen adsorption given in langmuirs. The spectra were taken at the $X(Y)$ point of the Brillouin zone with 21.22 eV photon energy (overall energy resolution of 25 meV, $T < 20$ K) and are normalized by constant photon flux. The measuring time for the whole series was about 1 hour.

cleavage. Besides the intense surface-derived state at 0.92 eV binding energy lying on a broad emission onset of bulk bands the spectrum consists of broad emission starting at the Fermi energy (0 eV binding energy). After an amount of 0.02 L hydrogen the intensity of the surface peak is already decreased and after 0.5 L the intensity has decreased dramatically. The uppermost spectrum was recorded shortly after the 0.5 L one, but with the sample having been heated to 50 K for a few minutes (flashing) and cooled to below 20 K again. By this procedure it became possible to desorb most of the hydrogen from the surface, controlled by a mass analyzer, the surface peak is found to be almost totally recovered. Note

that, similar to the previous contamination experiments, all additional emission is not affected by the adsorbed hydrogen.

The appearance of a surface-derived state indicates a redistribution of charge in the surface. This can be explained by the fact that cleavage of $YBa_2Cu_3O_{7-\delta}$ requires the breaking of strong bonds between the layers. In particular, for a Ba–O(4) termination with a Cu(1)–O(1) sublayer, which is the only non-polar one, marked changes have been theoretically proposed by Calandra et al. [7, 8] in the surface density of states in comparison to the bulk. X-ray photoemission [13] and photoemission experiments in the constant-final-state mode [14] show shifted components of the Ba core levels, which are interpreted to represent a Ba surface species. From our photoemission investigations we would conclude that the cleavage plane consists of Ba–O(4) and Cu(2)–O(2,3) domains. This seems to be the easy cleavage plane of $YBa_2Cu_3O_{6.8}$.

In summary, the observation of a surface-derived band on the Ba–O(4)/Cu(2)–O(2,3) face ("normal" cleavage plane) of $YBa_2Cu_3O_{6.8}$, indicating a rearrangement of electronic charge at the surface probably explains why in this compound no superconducting gap could be detected by photoemission (or scanning tunneling spectroscopy, STS) so far. The very recent evidence for the possibility of a second cleavage plane in this compound reported in Ref. [12] is interesting and needs further experimental work, but also shows that spectroscopic experiments on $YBa_2Cu_3O_{7-\delta}$ are much more complicated than on the previously studied $Bi_2Sr_2CaCu_2O_{8+\delta}$ system. On the other hand, Fermi edges and dispersing bands have been detected on surfaces where the 0.9 eV surface peak was realized. Hence, a mapping of bulk-derived bands by ARPES remains to be a meaningful experiment.

Acknowledgement

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