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Surface study of the 83-K superconductor $Bi_2Sr_2CaCu_2O_8$ by low-energy electron diffraction and angle-resolved inverse photoemission spectroscopy

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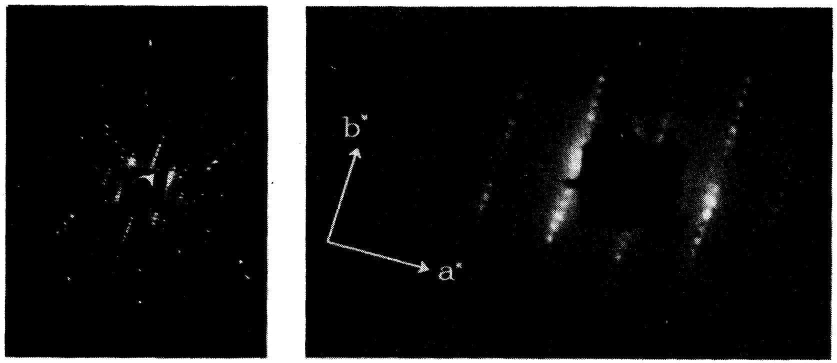
Low-energy electron diffraction (LEED) and angle-resolved inverse photoemission spectroscopy (ARIPES) have been applied to the cleaved surface of $Bi_2Sr_2CaCu_2O_8$ single crystals. The LEED pattern shows a surface lattice which is identical to the superlattice found in the bulk structure. ARIPES along the $\Gamma X(a^*)$ direction yields nondispersive unoccupied electronic states at 2.9 and ~5 eV above the Fermi energy attributed to Bi-O derived conduction bands. At about $\frac{1}{2}\Gamma X$ the experimental density of states at the Fermi level increases. This may be due to the crossing of the O(1) band through E_F, derived from oxygen atoms in the Cu-O planes.

The recently discovered 83-K superconductor $Bi_2Sr_2CaCu_2O_8$ (Ref. 1) has been the subject of many investigations concerning both geometrical[2-10] and electronic[11-18] structure. While x-ray diffraction and transmission electron diffraction have been used to study the crystal structure of the bulk, the electronic structure has been probed by photoemission spectroscopy (PES),[11-15] inverse photoemission spectroscopy (IPES),[12] x-ray absorption spectroscopy (XAS),[16] and electron energy-loss spectroscopy (EELS).[17,18] With the exception of EELS these techniques are surface-sensitive spectroscopies. The goal of this study is to investigate the relationship between the bulk and surface structure of single-crystalline $Bi_2Sr_2CaCu_2O_8$ using Laue diffraction and low-energy electron diffraction (LEED). We are able to identify the observed LEED spots with highly symmetric directions in the Brillouin zone using a face-centered unit cell in line with recent band-structure calculations.[19-23] The unoccupied part of the band structure has been measured by *angle-resolved* inverse photoemission spectroscopy (ARIPES) up to 9 eV above the Fermi level along the high-symmetry directions of the Brillouin zone.

The preparation of the $Bi_2Sr_2CaCu_2O_8$ single crystals is described elsewhere.[24] From ac magnetic susceptibility a T_c of 83 K is determined. From x-ray diffraction it is concluded that the samples consist dominantly of the $n=2$ phase.[25] The good chemical stability of the samples is demonstrated by the fact that we did not observe any time dependence of the ARIPES spectra as may be due to, e.g., oxygen loss. The samples were introduced into an ultrahigh vacuum chamber and cleaved *in situ* after moderate baking (T 100 °C) at a base pressure in the low 10^{-10} Torr range. The samples had a size of typically 2×3 mm^2. Details of the angle-resolved inverse photoemission spectrometer can be found in Refs. 26 and 27. The photon detector operates at an energy of 9.9 eV, the overall energy resolution of the spectrometer is 640 meV. Wave-vector resolution is estimated to be smaller than 0.1 Å^{-1}. The Fermi edge of a sputtered polycrystalline gold film is used as energy reference. Both LEED and ARIPES measurements have been carried out at room temperatures.

Figure 1(a) shows a Laue photograph obtained by x-ray back reflection using a Phillips PW 1720 x-ray generator with a tungsten anode at 35 kV. The sample was oriented with the macroscopic cleavage plane perpendicular to the incident x-ray beam. The diffraction pattern shows a mirror plane and a splitting of spots outside this plane. The observed splitting can be explained by the sample consisting of several single crystals with their c axis slightly tilted with respect to one another within the mirror plane. This may be due to an inequivalence of the two high-symmetry directions in the cleavage plane and has to be correlated to the observation of a one-dimensional superstructure along the b^* direction in the bulk structure.[2-6]

Figure 1(b) shows a LEED pattern obtained from the sample of Fig. 1(a) using a primary electron energy of 80 eV. We observe a rectangular pattern with a high density of spots along the direction denoted by b^*, which is identical with the direction of the mirror plane in the Laue photograph. When interpreted in terms of a primitive rectangular surface lattice the LEED pattern leads to lattice parameters of $a=5.4$ Å and $b=27.3$ Å. Studies of the bulk structure found an orthorhombic subcell with dimensions $5.41\times5.44\times30.78$ Å^3 and a b-axis superstructure of 27.2 Å (Ref. 2). Concerning the origin of the superstructure it has been speculated that it may be due to ordering of the short Bi-O bonds within the Bi-rich layers.[3,4] A recent transmission electron microscopy study by Zandbergen *et al.*[10] compares computer calculated images using different superlattice models to experimental data. They obtain best agreement for a model in which extra oxygen is incorporated in the Bi-O layers relieving the lattice mismatch between the Bi-O plane and the underlying perovskite blocks. From the large bond length of ≈3 Å between adjacent Bi-O planes[3,4] and the fact that band-structure calculations find vanishing charge density be-



(a) (b)

FIG. 1. (a) Laue photograph of a $Bi_2Sr_2CaCu_2O_8$ single crystal; notice mirrorlike symmetry. (b) LEED pattern obtained from the cleaved surface of the same sample at a primary electron energy of 80 eV.

tween them it may be concluded that cleavage occurs here. This view is supported by the observation of Bi-derived electronic states in the strongly surface sensitive inverse photoemission spectroscopy (see below). Thus, we find a consistent explanation for the observed LEED pattern. Since we are not able to distinguish spots attributable to the underlying 1×1 bulk structure from the 5×1 superlattice we conclude that the superstructure is fully developed in the surface layer. This strongly supports the aforementioned speculations attributing the superstructure to atomic rearrangement in the Bi-O planes. Our results are in very good agreement with scanning tunneling microscopy (STM) measurements.[8,9] The results of tunneling spectroscopy obtained by Tang *et al.*[8] compared to calculated density of states suggests that the surface layer is identical to the Bi-O plane, while Kirk *et al.*[9] also find a one-dimensional superstructure of periodicity 27.3 Å.

The identification of LEED spots with high symmetry directions in the crystal was used for the orientation of the samples in ARIPES. Figure 2(a) shows a series of ARIPES spectra for varying angles of electron incidence along the a^* direction, which corresponds to the ΓX line of the Brillouin zone of recent band-structure calculations.[19-23] Since this direction is not affected by the superstructure we may compare the experimental results with the calculations. At normal incidence ($\vartheta = 0°$) we observe a distinct feature denoted by A at 2.9 eV above the Fermi level. When going to higher angles of incidence peak A decreases in intensity but, within experimental uncertainty, does not show any considerable energy dispersion. In addition, at higher angles a broad but clear emission (B) evolves at about 4.5–5.0 eV. Because of the absence of distinct dispersion our spectra are in good agreement with IPES data on polycrystalline samples.[12] A recently calculated IPES based on the theoretical total density of states (DOS) using a photon energy of 18 eV (Ref. 28) yields an intensity peak at 2.4 eV above E_F. Thus, peak A has to be attributed to the antibonding hybrids of Bi 6p orbitals with O(2) and O(3) p states in the Bi-O and Sr-O planes, respectively.[21] This interpretation of our peak A is strongly supported by XAS (Ref. 16) and EELS (Ref. 17) results. They find a characteristic absorption onset due to the excitation from the O 1s core level to an oxygen-derived state at 2 eV above E_F. From the polarization dependence of the XAS and from the wave-vector dependence of the EELS spectra it can be derived that both in-plane [Bi-O(2)] and out-of-plane [Bi-O(3)] bonding contribute to this conduction-band state. The broad emission B of our ARIPES spectra may correspond to the upper conduction band of the band-structure calculation of Ref. 21. A similar emission is found in the IPES on a polycrystalline sample by Michel *et al.*[12]

Apart from intensity modulation due to matrix element effects features A and B do not show any considerable k dependence of their energy location. This is in strong disagreement with band-structure calculations which pre-

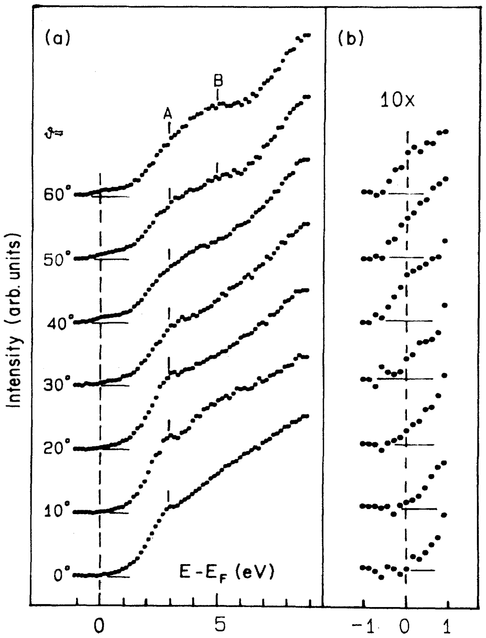


FIG. 2. (a) Series of ARIPES (original data) for various angles of electron incidence along the a^* direction, intensities are normalized to the incident electron charge. (b) Emission near the Fermi level, notice magnified scale.

dict a dispersion for the Bi-O(2) derived conduction band along ΓX as high as 3 eV.[19-21] Rather, our spectra strongly resemble the calculated *total* density of empty states despite the clear single-crystalline character of the samples. The absence of k dispersion may be taken as a hint that electronic correlation effects are also in the Bi-O planes of greater importance than previously assumed.

When following the spectra from low to high angles of incidence we find between $\vartheta = 30°$ and $40°$ an increase of intensity at the Fermi energy. Figure 2(b) shows the original data near E_F normalized to the incident electronic charge. With a work function of 5.3 eV as derived from photoemission data[15] this increase appears between 0.55 and 0.70 Å^{-1} corresponding to about $\frac{1}{2}\Gamma X$. This can be compared to the value of $0.4\Gamma X$ which the band theories predict for the crossing of the antibonding Cu-O band through the Fermi level. But it should be mentioned here that, according to experimental investigations, close to E_F the contribution of Cu $3d$ states is found to be very weak, both above and below, and that neither the present inverse photoemission study nor previous photoemission work[11,15] confirm the theoretically predicted dispersion of up to 3 eV for this band. All these observations point to stronger on-site Coulomb repulsion of the Cu $3d$ electrons than accounted for by LDA calculations, acting to push them away from E_F. Regarding the character of the unoccupied states near the Fermi level already the calculated IPES of Ref. 28 based on the total DOS shows that the finite intensity near E_F is attributed mainly to O(1) p states. Indeed, using photoemission spectroscopy in the constant-initial-state (CIS) mode[29] we found excitations from the O $2s$ core level to the unoccupied states close above the Fermi level leading to a core hole, whose relaxation couples resonantly to the direct photoemission. Since the photoexcitation process of the core electron is localized on the same atomic site, we conclude that the empty states must have O $2p$ character. Again, this is in good agreement with XAS (Ref. 16) and EELS (Ref. 17) results, where an excitation is observed from the O $1s$ level to O $2p$ states just above E_F having almost pure $p_{x,y}$ symmetry, which is the theoretically expected symmetry of the O(1)-derived bands. Thus, the increase in intensity found in the ARIPES spectra should be interpreted as due to the O(1) band dispersing through the Fermi level. This clearly confirms the existence of a Fermi surface at room temperature in $Bi_2Sr_2CaCu_2O_8$.

We also performed ARIPES along the b^* direction. For the peaks A and B we find the same energy locations and intensity variations as along the a^* direction. At the Fermi level we have no conclusive results, possibly because weak dispersion effects are obscured by the superstructure in the surface Bi-O layer, which leads to a surface Brillouin zone extension of 0.23 Å^{-1} along the b^* direction.

In conclusion we have performed surface measurements on the cleaved, single-crystalline (001) surface of $Bi_2Sr_2CaCu_2O_8$. We found from LEED a surface lattice with parameters $a = 5.4$ Å and $b = 27.3$ Å, which are identical to the superstructure parameters found in the bulk structure. ARIPES spectra show Bi-O derived conduction bands having no dispersion, while a band assigned to O(1) states seems to cross the Fermi level at a slightly larger $k_\parallel$ value than predicted theoretically. Both LEED and ARIPES results combined lead to the conclusion that the crystals are cleaved between adjacent Bi-O layers and that the superstructure is localized in the Bi-O planes.

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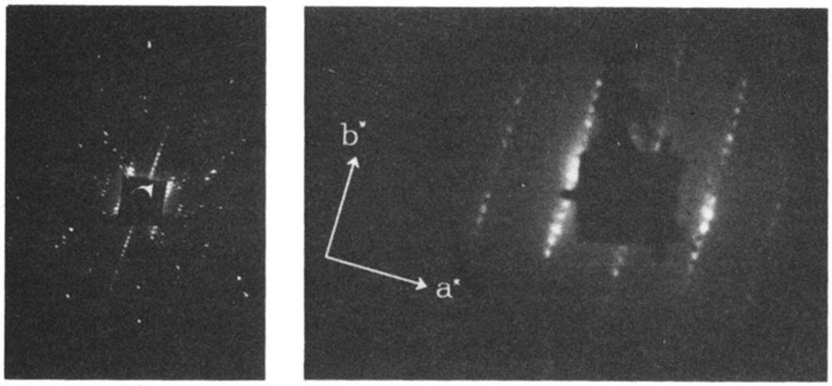

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