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SURFACE AND GRAIN BOUNDARY ANALYSIS OF HIGH TEMPERATURE SUPERCONDUCTORS

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Abstract:

The purpose of this paper is to survey the methods that are available for probing surfaces and grain boundaries of high temperature superconductors. Various surface-sensitive spectroscopies are applied to the analysis of $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ including photoelectron spectroscopy, spatially-resolved electron energy loss spectroscopy, and scanning electron microscopy (SEM). One of the major sources of contamination at surfaces and grain boundaries is found to be $BaCO_3$. The cleavage surface of single crystal $Bi_2Sr_2CaCu_2O_{8+x}$ is inert and can be used to probe bulk properties of superconductors, even with surface-sensitive techniques. The orbital character of the superconducting oxygen 2p holes is found to be $p_{x,y}$, with x,y in the a,b plane. Photoemission at the Fermi level indicates a Fermi liquid nature of these states.

Key words: High temperature superconductors, photoelectron spectroscopy, energy loss spectroscopy, surfaces, grain boundaries

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Introduction

After the initial excitement produced by the discovery of high temperature superconductivity in ceramic oxides, it has been found that good mechanical properties and high critical currents are difficult to attain in bulk materials. This is the result of several factors that are poorly understood; namely, densification mechanisms, grain orientation, grain boundary phases. All these factors underscore the need to focus on the surface and interfacial properties of these materials. Thus, a strong effort is currently being made to address these issues using techniques that can probe the surface or grain boundaries of materials.

The low critical current densities of polycrystalline $YBa_2Cu_3O_7$, as compared to the values attained in epitaxial films and in single crystals, have generally been attributed to critical current anisotropy and poor coupling across the grain boundaries (Chaudhari et al. (1987), Camps et al (1987), Clarke (1987)). To address this issue, Dimos et al.(1988) have performed critical current measurements on epitaxial films grown on $SrTiO_3$ bicrystals produced by sintering two misoriented single crystals. The films were patterned in such a way that they allowed the measurements of current-voltage characteristics in two single grain regions and across the grain boundary in the same film. These measurements revealed that the grain-boundary critical current density decreases with misorientation angle. However, the lowest of these values is still an order of magnitude higher than the critical current densities typically measured in polycrystalline bulk samples($\simeq$1-5 $\times 10^3 A/cm^2$). This discrepancy suggests that other factors may be affecting the transport properties of the bulk oxide superconductors. Clarke (1987) has proposed that grain boundary phases, which may arise from reaction with contaminants or from a different stoichiometry, may play an important role in decreasing the critical current density. Evidence of extra phases can be found in the transmission electron microscopy (TEM) work produced by Camps et al. (1987), and in early photoemission studies of the polycrystalline oxide superconductors; for instance, those appearing in the work by Miller et al.(1988).

Polycrystalline $YBa_2Cu_3O_7$: Surfaces, Grain Boundaries

While photoemission spectroscopy can be a good technique for probing bonding, composition and oxidation states in these materials, the surface sensitivity of the technique (0.5-3 nm) requires that the surface preparation of the materials be carefully scrutinized so as to ensure that the observed spectra are representative of the bulk material. Many of the discrepancies are now being clarified with more reliable data from in-situ cleaved single crystals. It turns out that in most cases, there were spurious signals due to the presence of Ba-hydroxide and carbonate. The hydroxide can generally be attributed to poor storage of the sample prior to analysis, or poor vacuum conditions, while the carbonate phase seems to be related to processing conditions.

Representative oxygen 1s core level photoemission spectra of $YBa_2Cu_3O_7$ are shown in Fig. 1. All spectra from polycrystalline $YBa_2Cu_3O_7$ show at least two distinct peaks observed at binding energies of 528.5 and 531.3 eV. However the relative intensities of these features are strongly dependent upon the method of sample preparation and on the escape depth of the experiment. Figure 1a depicts the oxygen 1s spectrum of an in-situ fractured ceramic sample taken with synchrotron radiation at an escape depth of about 0.5 nm. The 531.3 eV peak is significantly more intense than the peak at 528.5 eV (ratio of 4.2:1). When a sister sample is fractured and analyzed with X-ray photoelectron spectroscopy (XPS) (Fig. 1b), the intensity ratio of the 531.3 to 528.5 eV peaks decreases to approximately 1.4:1.In this case, the inelastic mean free path is greater ($\simeq$ 1.5 nm) due to the higher kinetic energy of the outgoing electrons. Since the intensity of this 531.3 eV peak is higher in the more surface sensitive experiment, it appears that it corresponds to material segregated at the fractured surface. The most likely assignment is $BaCO_3$, based on the correlation of the oxygen 1s feature with a carbon 1s feature which exhibits an energy shift of $\simeq$ 5 eV from that of graphite, due to carbon-oxygen bonding (Schrott et al.(1988)). A small portion of the 531.3 eV oxygen 1s feature could also be due to $Ba(OH)_2$.

If the fractured surface analyzed in Fig. 1b is subsequently scraped, the relative intensity of the two peaks changes once again. Figure 1c shows the effects of extensive scraping of these samples in vacuum at 160°K

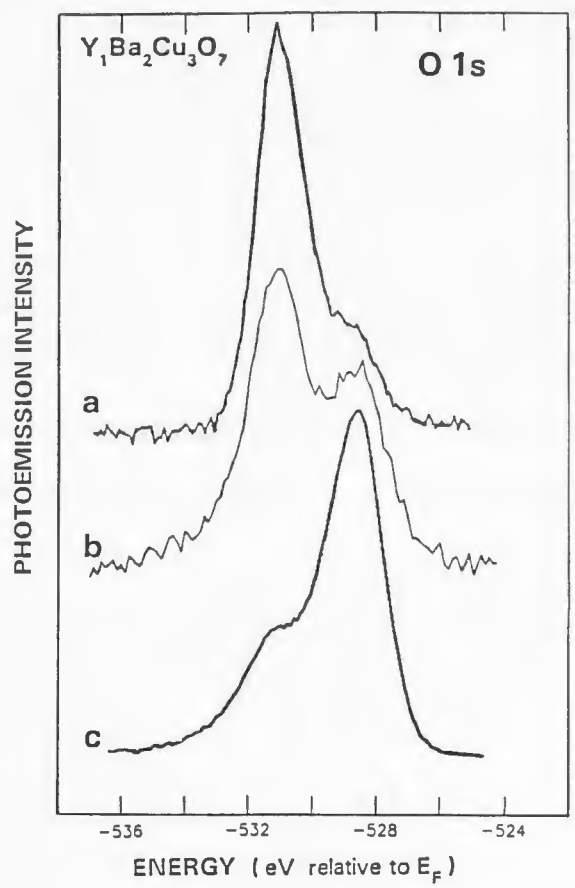

Fig. 1. Oxygen 1s photoemission spectra for $YBa_2Cu_3O_7$. (a) Fractured sample, $h\nu \sim 700$ eV; (b) fractured sample, $h\nu = 1253$eV; (c) well scraped sample, $h\nu = 1253$ eV. From Schrott et al.(1988).

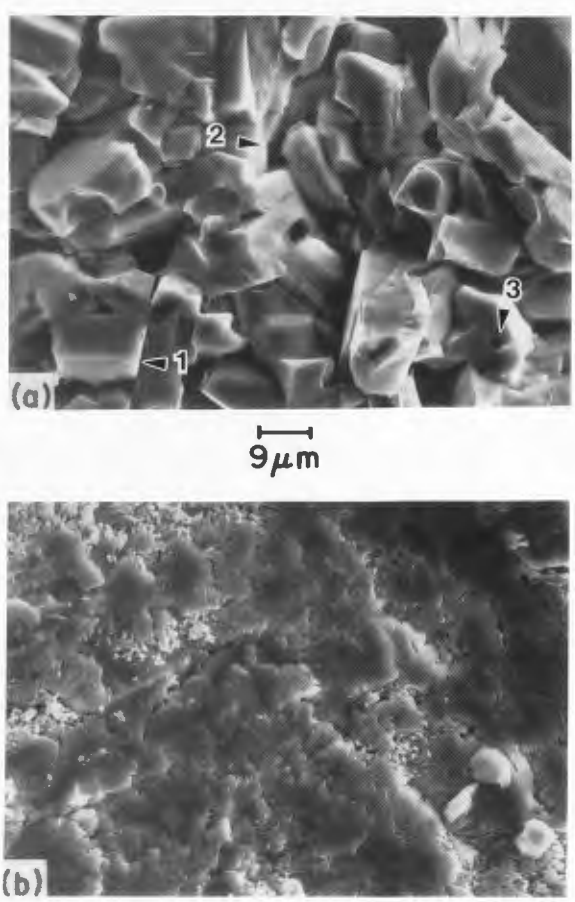

Fig 2. SEM micrographs of $YBa_2Cu_3O_7$. (a) Fractured sample, (b) scraped sample. From Schrott et al (1988).

leading to large decrease of the oxygen 1s peak at 531.3 eV. Scanning electron microscopy (SEM) images from a fractured and a scraped surface are shown in Fig. 2, and help to understand the differences between the spectra shown in Figs. 1 b and c (Schrott et al. (1988)). Clearly, the surface of a fractured $YBa_2Cu_3O_7$ specimen is radically different (Fig. 2a) from that of the surface of the scraped sample (Fig. 2b).

The SEM micrograph of the fractured $YBa_2Cu_3O_7$ surface is indicative of both intergranular and intragranular fracture. The intergranular regions of the fracture surface are characterized by highly faceted grains (arrow 1 in Fig. 2a). In addition, large areas of residual porosity exist at the multi-grain junctions (arrow 2 in Fig. 2a).

In contrast to the intergranular regions, the regions of intragranular fracture were characterized by entrapped porosity which displayed a circular cross-section (arrow 3 in Fig. 2a). Although detailed quantitative microscopy was not attempted on these materials, Cook et al.(1987a) suggested that the percentage of intergranular fracture for a pressureless sintered material is about 50 per cent. This value is undoubtedly dependent on the processing and thermal histories of the sample and is critically dependent on the presence of an intergranular phase. The amount of intergranular fracture in the present case appears to be consistent with this value.

The scraped surface was relatively flat indicating that more intragranular fracture had occurred than in the fractured specimen, thus giving a more representative section of the microstructure. Considerable wear debris was present on the scraped surface and it tended to collect in pockets of residual porosity. Also apparent on the scraped surface were areas which appeared to have been plastically deformed. Fracture toughness measurements of single crystals of $YBa_2Cu_3O_7$ by Cook et al. (1987b) indicate that the fracture toughness of this material is quite low with $K_c = 1.1 \pm 0.3 MPam^{1/2}$. In light of this result, the occurrence of a plastic mode of deformation seems unlikely, and it is more probable that the "apparent" plastic deformation is simply the filling of porosity with fine wear debris.

No evidence for a secondary grain boundary phase was observed using Energy Dispersive X-ray Spectroscopy (EDXS). This technique, however, is not sensitive to thin surface layers and the contribution of the grain boundary phase in this case is not significant enough to detect. Since the SEM images of the scraped surfaces suggest the presence of significant regions of intragranular fracture, the scraped surfaces would be more representative of the bulk in these superconducting oxides.

The presence of a carbonate containing grain boundary phase in $YBa_2Cu_3O_7$ will also influence the valence band photoemission spectra. This is illustrated in Fig. 3 by comparing the valence band photoemission spectra of (a)$BaCO_3$ with analogous spectra of(b) fractured and (c) scraped $YBa_2Cu_3O_7$. Figure 3c corresponds to the same sample as Fig. 1c. There is a strong

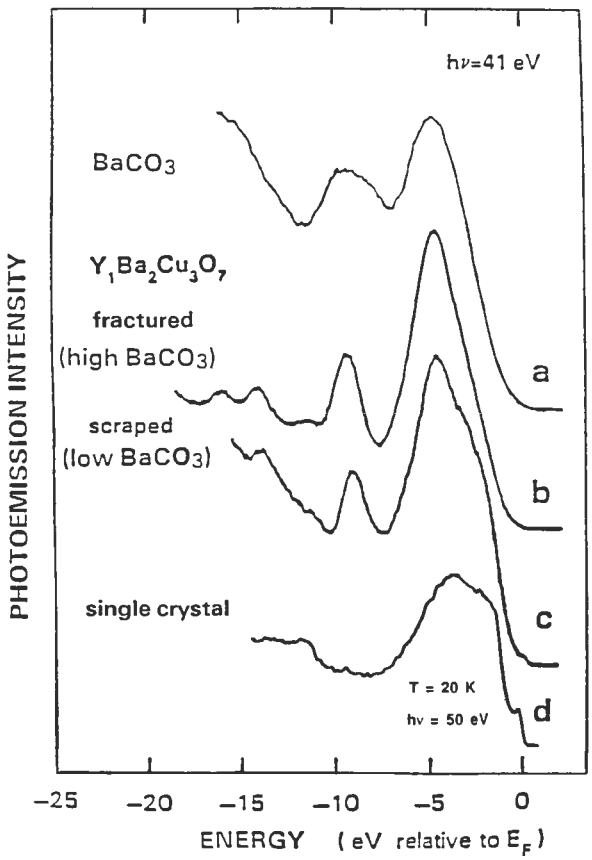

Fig. 3. Photoemission spectra of: (a) $BaCO_3$, (b)in-situ fractured polycrystalline $YBa_2Cu_3O_7$; (c) in-situ scraped polycrystalline $YBa_2Cu_3O_7$; (d) in-situ fractured $YBa_2Cu_3O_7$ single crystal, from Arko et al. (1989).

resemblance between the spectra of polycrystalline $YBa_2Cu_3O_7$ and $BaCO_3$ as seen in Fig. 3. The energy splitting of the two main features at ~ 5 and 9 eV are quite similar in these two materials. (There is a 0.7 eV shift to deeper binding energy for the lowest binding energy $BaCO_3$ feature relative to the analogous peak in $YBa_2Cu_3O_7$) Thus, in the presence of significant amounts of $BaCO_3$, (i.e. on the fractured surface), it is difficult to determine the intrinsic line shape of the $YBa_2Cu_3O_7$. The scraped surfaces (Fig. 3c), which have lower levels of $BaCO_3$ impurity exhibit somewhat different valence band spectra from that of the fractured surfaces. A pronounced shoulder appears at lower binding energy (2-3 eV) and a sharp Fermi edge is observed. The observation of a Fermi edge suggests that the scraped surfaces might be more representative of the bulk of the material (which is metallic) in agreement with the SEM and XPS analyses.

The feature at $\simeq$ 9 eV has been observed in all valence spectra of the polycrystalline $YBa_2Cu_3O_7$ materials. Since there is a $BaCO_3$ peak at this binding energy the intensity of this feature will clearly depend on the amount

of surface carbonate impurity. Additional sources contributing to the 9 eV feature are BaOH or defects in the surface oxygen stoichiometry. There have been claims that this feature is intrinsic to $YBa_2Cu_3O_7$. For example, valence spectra from $YBa_2Cu_3O_7$ single crystals cleaved (and measured) at liquid nitrogen temperature, exhibit the feature at $\simeq$ 9 eV (Tang et al. (1988)). However, more recent single crystal data, obtained by Arko et al. (1989) below 30 K (Fig 3d), do not exhibit this feature, and have a more pronounced metallic Fermi edge, representative of the metallic nature of $YBa_2Cu_3O_7$.

Although photoemission studies can provide information on the nature of possible grain boundary phases in oxide superconductors with good depth resolution, it averages over the area detected by the spectrometer, typically of the order of a mm^2. High spatial resolution (in the order of 0.5 x 0.5 nm^2) can be achieved by Electron Energy Loss Spectroscopy (EELS) studies.

Figure 4 shows energy loss spectra obtained by Batson et al.(1989) from a grain boundary filled with a glassy phase. The loss spectra near the carbon 1s-edge for the unknown carbon containing phase, for amorphous carbon, $BaCO_3$ and $CuCO_3$ are shown in Fig. 4a. Although the spectra for $BaCO_3$ and $CuCO_3$ are similar, a good correspondence between the glassy phase and $BaCO_3$ can be made on the basis of the position of the narrow resonance near 290 eV. This is consistent with the correspondence found for the oxygen 1s edges shown in Fig. 4 b. The high spatial resolution of this technique allows for studies in which a correlation can be made between processing parameters, rate of diffusion of oxygen and carbon, and the electrical properties of the polycrystalline oxide superconductors.

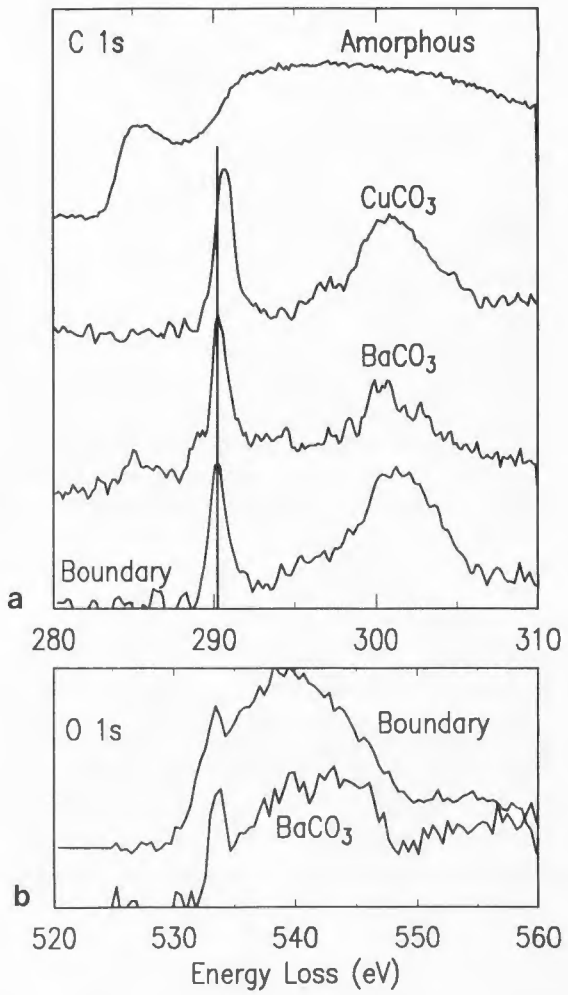

Fig 4. EELS spectra polycrystalline $YBa_2Cu_3O_7$.(a) Comparison of the carbon 1s-edge for a grain boundary region whith those of amorphous carbon, $CuCO_3$, and oxygen $BaCO_3$; (b) Comparison of the oxygen 1s for the grain boundary phase with that of $BaCO_3$. From Batson et al.(1989).

Single Crystal $Bi_2Sr_2CaCu_2O_{8+x}$

For probing bulk properties of high temperature superconductors, it is important that the effect of surface and grain boundary phases be mininized. This holds particularly for techniques like photoelectron spectroscopy, which give the most complete picture of the electronic structure, but exhibit a built-in surface sensitivity due to the short escape depth of the photoelectrons. The first step is, of course, to use single crystals material instead of ceramic material. From the findings in the previous section one also would want to avoid barium containing compounds, because of the strong tendency of BaO to form BaOH and $BaCO_3$. The structure of $Bi_2Sr_2CaCu_2O_{8+x}$ (and $Tl_2Ba_2CaCu_2O_{8+x}$) is optimally-suited for this purpose. They cleave readily (along the a,b plane) and the cleavage surface turns out to be chemically inert, similar to layered compounds like graphite and MoS_2. A possible reason for this may be the existence of a unique symmetry plane (between the BiO layers) which allows one to create two identical surfaces by cleaving. For the 123 compounds such a symmetry plane does not exist, and one will always produce a high energy surface together with a low energy surface during cleaving. An additional simplification arises from the fact that these compounds exhibit only one type of CuO_2 planes, not chains and planes, like the 123 compounds. Two key results about the electronic structure of high temperature superconductors will be discussed in the following, i.e. the orbital character of the superconducting holes and the observation of a superconducting gap in photoemission.

We know that holes (and not electrons) are responsible for superconductivity from the correlation that has been established between the transition temperature T_c and the hole concentration, as measured by wet chemistry and the Hall effect. Therefore, the study of unoccupied

states just above the Fermi level E_F is of prime interest to understanding the superconducting hole states. Such states can be studied with soft X-ray absorption (Yarmoff et al. (1987), Himpsel et al. (1988)) or by electron energy loss spectroscopy (Nucker et al. (1988)). Their atomic character is revealed by observing transitions from the core level of a particular atom into an empty state localized on that atom. At the Cu2p absorption edge, the transitions into the empty Cu3d states corresponding to the $3d^9$ configuration of Cu^{2+} have been observed. Upon doping, additional holes are created, which appear at the oxygen 1s edge, not at the Cu2p edge (Fig. 5). One can go a step further and determine the orbital symmetry (p-like for the oxygen states) and the orbital orientation ($p_{x,y}$ – like) by using dipole selection rules (Himpsel et al. (1988)). With the electric field vector **E** parallel to the x axis only transitions into p_x orbitals are allowed from an s level, and likewise for the other directions. For single crystals of $Bi_2Sr_2CaCu_2O_{8+x}$ cleaved along the ab-plane, one finds that the oxygen p holes are excited by **E** parallel to the surface (Fig. 5) Thus, they have $p_{x,y}$ character with x, y in the superconducting a,b plane. For $YBa_2Cu_3O_{7-x}$, similar experiments have been performed. However, unoccupied oxygen states with $p_{x,y}$ as well as with p_z character have been found, reflecting the existence of chains and planes of CuO.

There is a natural explanation for the $p_{x,y}$ character of the oxygen p holes, using a widely-adopted bonding concept for the CuO_2 planes. The $Cu3d_{x^2-y^2}$ orbital has lobes pointing towards the in-plane oxygen that interact strongly with the oxygen $2p_{x,y}$ orbitals. Their antibonding combination represents the highest occupied orbital, and will be the first one to be depleted when creating holes via doping. Note that there are two types of oxygen $2p_{x,y}$ orbitals, one along the Cu-O bonds, the other perpendic-

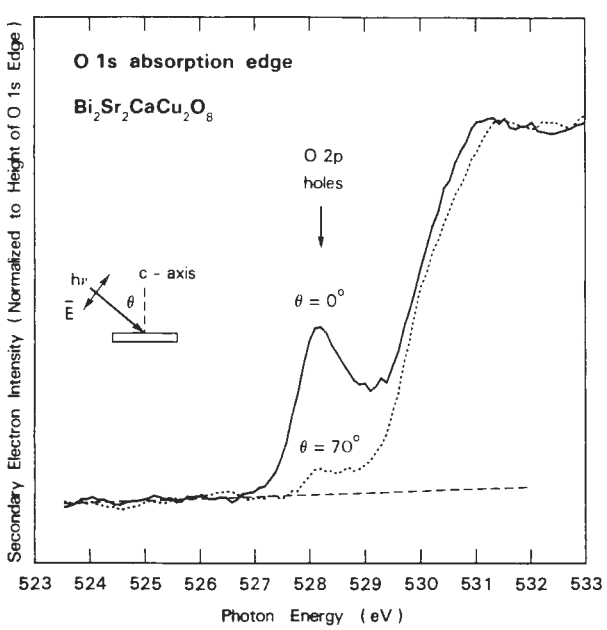

Fig 5. Transitions from the oxygen 1s core level into empty oxygen 2p states observed at the oxygen 1s absorption edge. From the polarization dependence one deduces $p_{x,y}$ orbital character, with x,y parallel to the a,b-plane. After Himpsel et al. (1988).

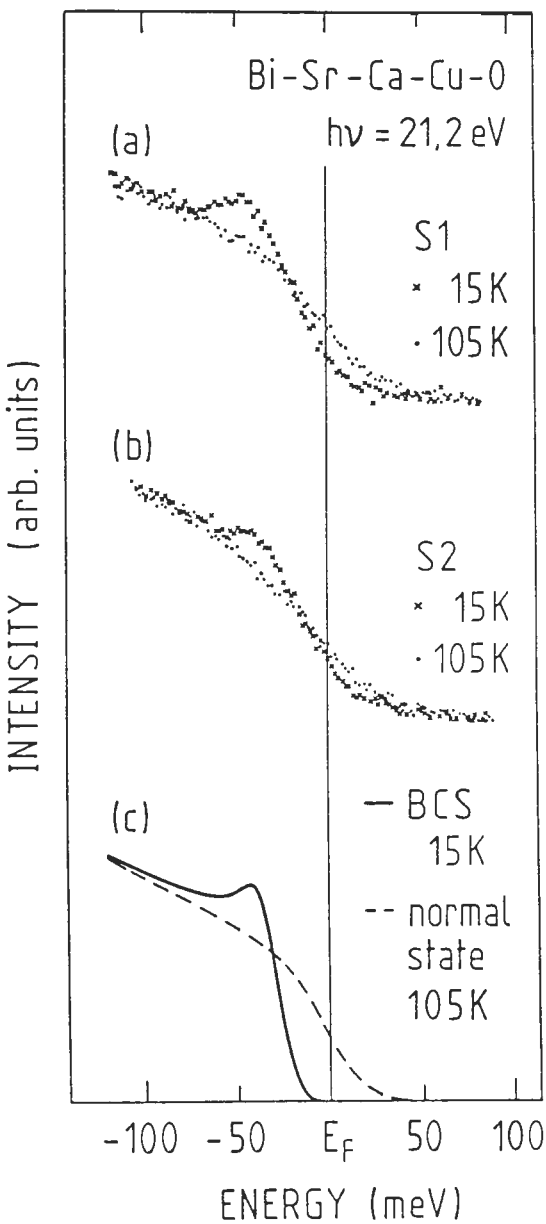

Fig. 6. Photoemission spectra from $Bi_2Sr_2CaCu_2O_{8+x}$ above and below T_c for two samples (S1 and S2). The opening of a superconducting gap is modeled in (c). From Imer et al. (1989).

ular to it. In the standard model the oxygen 2p holes are located in the Cu-O σ-bond, but the possibility of having the holes in the perpendicular π-bonding orbital has also been proposed. The polarization experiment averages over these two directions and cannot distinguish between them. However, one can rule out a π-bond formed by the p_z orbital as location of the holes.

The principal change in the electronic structure below the critical temperature is the opening-up of a superconducting gap, which corresponds to the energy to break up Cooper pairs. The observation of this gap with photoelectron spectroscopy has long been sought after, but has become reality only recently with the high temperature superconductors (Fig. 6 and Chang et al. (1989), Imer et al. (1989), Olson et al. (1989)). Although it is difficult to detect such a gap with a high energy spectroscopy, like photoemission, there is the extra capability of resolving the momentum. From the distribution of the gap in momentum space one should be able to gather extra information about the yet unknown pairing mechanism. The spectra shown in Fig. 6 (from Imer et al. (1989)) represent the state of the art in high-resolution photoemission, about 0.02eV energy resolution. After taking the finite resolution and the Fermi-Dirac distribution near the Fermi level E_F into account, the spectra can be modeled by a gap $\Delta = 0.03$eV appearing below E_F when cooling below T_c. The total gap (including an equal contribution above E_F) is $2\Delta = 0.06$ eV $= 8kT_c$, which is substantially larger than expected from standard BCS theory in the weak coupling limit, i.e. $2\Delta_{BCS} = 3.5\ kT_c$. The data in Fig. 6 were obtained in a momentum-integrating geometry. However, momentum-resolved data are being collected (Olson et al. (1989)) and promise to provide a complete picture of the electronic states near the Fermi level, which are essential for superconductivity.

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References

Arko AJ, List RS, Bartlett RJ, Cheong SW, Fisk Z, Thompson JD, Olson CG, Yang AB, Liu R, Gu C, Veal BW, Liu JZ, Paulikas AP, Vandervoort K, Claus H, Campuzano JC, Schriber JE, Shinn ND (1989) Large, dispersive photoelectron Fermi edge and the electronic structure of $YBa_2Cu_3O_{6.9}$ single crystals measured at 20 K. Phys. Rev. B40, 2268-2277.

Batson PE, Chisholm MF, Clarke DR, Dimos D, Shaw T (1989) Energy loss studies of carbon content in yttrium barium cuprate. In: Proceedings of the 47th Annual Meeting of the Electron Microscopy Society of America, Bailey (ed), San Francisco Press, San Francisco, in press.

Camps RA, Evetts JE, Glowacki BA, Newcomb SB, Somekh RE, Stobbs WM (1987) The microstructure and critical current of superconducting $YBa_2Cu_3O_{7-x}$. Nature 329, 229-232.

Chang Y, Tang M, Zanoni R, Onellion M, Joynt R, Huber DL, Margaritondo G, Morris PA, Bonner WA, Tarascon JM, Stoffel NG (1989) Theoretical and experimental analysis of the superconducting transition effects on the Fermi-edge photoemission spectra. Phys. Rev. B39, 4740-4743.

Chaudhari P, LeGoues FK, Segmuller A (1987) The microstructure of high-critical current superconducting films. Science 238, 342-344.

Clarke DR (1987) The development of high-T_c ceramic superconductors: an introduction. Adv. Ceram. Mat. 2, 273-287.

Cook RF, Shaw TM, Duncombe PR (1987a) Fracture properties of polycrystalline $YBa_2Cu_3O_x$.Adv. Ceram. Mat. 2, 606-614.

Cook RF, Dinger TR, Clarke DR (1987b) Fracture toughness measurements of $YBa_2Cu_3O_x$ single crystals. Appl Phys. Lett. 51, 454-456.

Dimos D, Chaudhari P, Mannhart J, LeGoues FK (1988) Orientation dependence of grain-boundary critical currents in $YBa_2Cu_3O_{7-\delta}$ bicrystals. Phys. Rev. Lett. 61, 219-222.

Himpsel FJ, Chandrashekhar GV, McLean AB, Shafer M.W. (1988) Orientation of the O 2p holes in $Bi_2Sr_2Ca_1Cu_2O_8$. Phys. Rev. B38, 11946-11948.

Imer JM, Patthey F, Dardel B, Schneider WD, Baer Y, Petroff Y, Zettl A (1989) High resolution photoemission study of the low-energy excitations reflecting the superconducting state of Bi-Sr-Ca-Cu-O single crystals. Phys. Rev. Lett. 62, 336-339.

Miller DC, Fowler DE, Brundle CR, Lee WY (1988) Photoemission studies of sputtered thin films and bulk samples of the 1-2-3 high T_c superconductor. In: Thin Film Processing and Characterization of High-Temperature Superconductors, Harper JME, Colton RJ , Feldman LC (eds), American Institute of Physics Conf. Proc. NO. 165, New York, 336-348.

Nücker N, Fink J, Fuggle JC, Durham PJ, Temmerman WM (1988) Evidence for holes on oxygen sites in the high-T_c superconductors $La_{2-x}Sr_xCuO_4$and $YBa_2Cu_3O_{7-y}$. Phys. Rev. B37, 5158-5163.

Olson CG, Liu R, Yang AB, Lynch DW, Arko AJ, List RS, Veal BW, Chang YC, Jiang PZ, Paulikas AP (1989) Determination of the superconducting gap in Bi-Sr-Ca-Cu-O by high-resolution angle-resolved photoelectron spectroscopy. Science 245, 731-733.

Schrott AG, Cohen SL, Dinger TR, Himpsel FJ, Yarmoff JA, Frase KG, Park SI, Purtell R (1988) Photoemission study of grain boundary segregation in $YBa_2Cu_3O_7$. In: Thin film Processing and Characterization of High-Temperature Superconductors, Harper JME, Colton RJ, Feldman LC (eds), American Institute of Physics Conf. Proc. No. 165, New York, 349-357.

Tang M, Stoffel NG, Chen QB, LaGraffe D, Morris PA, Bonner WA, Margaritondo G, Onellion M (1988) Nature of the valence band photoemission features of single-crystal $YBa_2Cu_3O_{7-x}$. Phys. Rev. B38, 897-899.

Yarmoff JA, Clarke DC, Drube W, Karlsson UO, Taleb-Ibrahimi A, Himpsel FJ (1987) Valence electronic structure of $Y_1Ba_2Cu_3O_7$. Phys. Rev. B36, 3967-3970.