Angle-Resolved-Photoemission Study of $Bi_2Sr_2CaCu_2O_{8+\delta}$: Metallicity of the Bi-O Plane

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We have performed high-resolution angle-resolved-photoemission experiments on $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals with different annealing histories. By depositing a small amount of Au on the surface we were able to distinguish electronic states associated with the Bi-O surface layer. We found that the Bi-O atomic surface layer is metallic and superconducting for samples that were high-temperature annealed in oxygen but not for as-grown samples. The Cu-O plane is found to be superconducting in all samples.

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Recent photoemission results on high-temperature superconductors have received a great deal of attention from the condensed-matter-physics community.[1-8] Two of the most important issues have been understanding the nature of the low-energy excitations and the superconducting properties of the surface region.

Understanding the nature of the low-energy excitations is the key to describing the normal and superconducting state of the high-T_c materials. Several of the high-T_c materials have a parent compound which is an antiferromagnetic insulator that appears to fall into the category of materials where the usual Fermi-liquid description breaks down. The high-T_c superconductors are made by doping the parent compound to an appropriate level. In this doped region, the materials have some characteristics of a normal metal and there is great controversy as to the best description of the ground state and the low-energy excitations. There are two main approaches. The first starts with the picture of a highly correlated antiferromagnetic insulator and modifies this picture to describe a metal through doping.[5,6] Photoemission and inverse photoemission results show that this doping is not accomplished by simply adding holes (or electrons) to a lower (or upper) charge-transfer band. The doping process appears to add new states within the charge-transfer gap.[3,4] These doping states may be added in such a way as to reproduce the one-electron [local-density-approximation (LDA)] band-structure-calculated Fermi surface for the metallic compound. The second approach begins with the traditional single-particle picture and then attempts to add on the effects of the correlated electrons as a perturbation.[9] In either case the information about the low-energy excitations near E_F and their relation to the LDA-calculated Fermi surface are of major importance.

The quality and intrinsic nature of the surface has been of great importance to anyone trying to analyze photoemission results as well as other surface-sensitive techniques such as tunneling. There have been concerns that photoemission results may have no bearing on understanding superconductivity because the surface region probed may not be representative of the bulk due to surface cleanliness and defect problems. Furthermore, conventional continuous Ginzburg-Landau theory suggests that even an atomically perfect surface may not be superconducting as a consequence of the extremely short coherence length.[10] The observation of the opening of a superconducting gap in the $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) material[1,2,11] clearly demonstrates that, at least for this compound, photoemission does indeed sample a region of superconducting material. However, whether the atomic surface is superconducting has not been examined for materials with a coherence length as short as 3 Å.

In this Letter we present new results that shine light on the two important issues discussed above. We first provide information about the atomic character of the bands near E_F, which shows that the Fermi surface has Bi-O or Cu-O character at **k**-space positions that are consistent with the LDA calculation. This complements earlier angle-resolved-photoemission data which show that the experimental bands intersect the Fermi level at **k**-space locations predicted by the LDA calculation.[6] We also discuss the metallicity and the superconductivity of the surface atomic layer. Since the 2:2:1:2 material has been shown to cleave between adjacent Bi-O planes,[12] the intrinsic surface properties are closely linked with the character of the Bi-O states. We demonstrate that the surface atomic layer is metallic and superconducting, at least for samples annealed in oxygen. This is different from the results from scanning tunneling microscopy,[13,14] which have claimed that the surface layer is insulating. For as-grown samples, not annealed in oxygen, we do not find Bi-O states at the Fermi level, perhaps indicating that the STM results may be correct but not representative of the 2:2:1:2 material in general. The purpose of this Letter is to establish that the surface layer is metallic and superconducting in the properly oxygen-annealed samples. To establish this required exacting experiments to determine the presence of the superconducting gap under various conditions, but these data do not allow an accurate determination of the gap size. It is important that such a careful determination be made in the future.

High-resolution, angle-resolved-photoemission experiments were performed on the Ames/Montana ERG/Seya beam line on Aladdin. Experimental details are the same as in Ref. 1. As-grown $Bi_2Sr_2CaCu_2O_8$ crystals had a Meissner transition onset at 89 K. Some crystals were annealed in different partial pressures of O_2 to change their T_c. For this material, when the oxygen content increases, the density of states at the Fermi level increases, and the transition temperature decreases. In particular, we studied as-grown crystals ($T_c = 89$ K), and 12-atm-O_2-annealed crystals ($T_c = 80$ K). Further details on the growth and characterization of the crystals used is available elsewhere.[15] The crystals were cleaved in a vacuum of better than 5×10^{-11} Torr at 20 K. The Au evaporations were performed from a resistively heated tungsten basket while the superconductor was maintained at 20 K.

We first studied the 12-atm-O_2-annealed sample. We took spectra every 2° (about $\frac{1}{12}$ of the Brillouin zone) along the Γ-X, Γ-Y, and Γ-M directions. As the emission angle of the collected electrons was changed in order to step in **k** space along the Γ-X (or Γ-Y) direction, we observe a broad feature approximately 200 meV below the Fermi energy. This feature becomes larger, sharper, and moves closer to the Fermi energy as we move in **k** space away from Γ and finally disappears as it becomes unoccupied above the Fermi energy, similar to the figures in Ref. 6. The dispersion direction and the point where the band crosses the Fermi level are consistent with the LDA calculation of Massida, Yu, and Freeman.[16] Along Γ-M the band showed similar behavior except that the dispersion was slower and the peak never totally disappeared as the **k** value was changed out to the M point. Because the band structure is more complicated in this direction, we were not able to tell whether there are separate Cu-O and Bi-O bands as the LDA calculation suggests.[16] Figure 1 shows the photoemission spectra both above and below T_c at the **k**-space positions where the bands cross the Fermi level along Γ-X and Γ-M. As the sample enters the superconducting state, the spectral weight pulls back from the Fermi energy and piles up just below, as one would expect for a superconducting gap. In fact, for each direction where we detected states at the Fermi level we were able to see a superconducting gap open upon cooling the sample below its transition temperature.

We derived an experiment to directly determine whether any of the states at the Fermi level are associated with the Bi-O plane. As previously mentioned, the material cleaves, leaving a Bi-O surface layer with two Cu-O layers several angstroms deeper. Because of the surface sensitivity of photoemission, we expect little contribution to the spectrum from the second, deep Bi-O layer. We perturbed the surface by evaporating a small coverage of Au onto the surface of the 2:2:1:2 sample. Au was chosen because earlier experiments showed very little chemical reaction between Au and $Bi_2Sr_2CaCu_2O_{8+\delta}$; the core levels from the non-surface-layer atoms (Ca,Cu,Sr) exhibited no changes and the Bi states had a very small shift in binding energy.[17-19] Also, Au seems to grow fairly uniform layers as the superconductor peaks are attenuated quickly with the growth of the Au overlayer. The cold temperature of the superconductor should reduce the mobility of the deposited Au atoms making the Au less likely to form any islands or move to preferred adsorption sites. For this experiment we investigated very small coverages of Au, about 0.5 Å. A submonolayer coverage of Au, deposited at low temperatures, should consist of isolated Au atoms and should not be metallic, i.e, should not contribute any states at the Fermi level. In fact, we saw no evidence for new Fermi-level states upon deposition of Au.

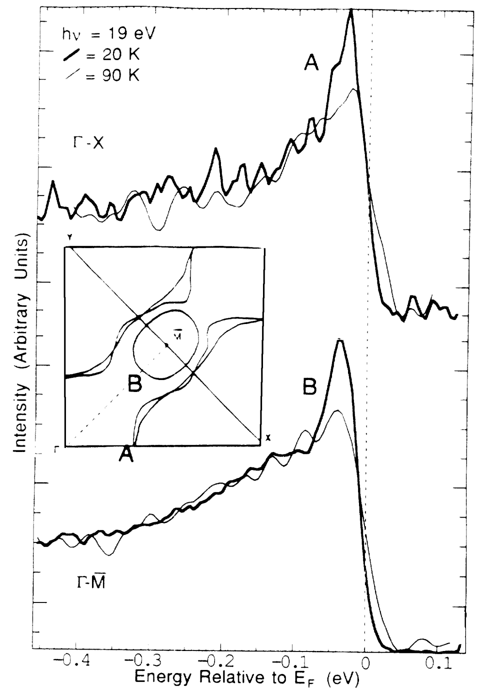

FIG. 1. Photoemission spectra showing the opening of a superconducting gap along both the Γ-X and the Γ-M directions in **k** space for the 12-atm-O_2-annealed sample. The Fermi surface is taken from Ref. 16.

It is important to note that the idea of using a surface contamination to identify surface states has been used before with great success. Surface states on GaAs can be destroyed without affecting the spectral shape or angular dependence of bulk features by exposing the surface to a small amount of O_2 or H_2.[20] The adsorbed atoms did not destroy the conservation of $\mathbf{k}_{\parallel}$ for electrons leaving the surface. Similar results were obtained for Si [21] and Ge. [22] The results of these earlier experiments coupled with the information we already know about the Au/2:2:1:2 interface leads us to believe that a small Au overlayer will be helpful in distinguishing states with a contribution from the surface layer.

We concentrated on the angles where the bands crossed the Fermi level, and compared the clean surface to the $\frac{1}{2}$-Å-Au-covered surface. Figure 2 shows the comparison of the clean and Au-covered $Bi_2Sr_2CaCu_2O_{8+\delta}$ along both the Γ-X and the Γ-M directions. Along the Γ-X direction there is no change in the line shape between the spectra from clean and Au-covered surfaces. In the Γ-M direction, however, it is clear that there has been a drastic change in the feature at the Fermi level —it is no longer visible. The experimental fact is that the two directions behave very differently; in one direction the Au overlayer has no effect on the underlying states while in the other direction it destroys the Fermi-surface states. Only the Cu-O and Bi-O layers should contribute any states at the Fermi level since the other layers are extremely ionic. It seems highly unlikely that the surface-adsorbed Au layers could disturb a deep layer (Cu-O) without affecting the surface (Bi-O). Even the core-level data mentioned above indicate that Au mainly affects the Bi-O states. Thus we assign the feature along the Γ-M direction to states from the surface, which therefore must have at least a significant proportion of Bi-O character. However, note that this experiment does not rule out the possibility of some Cu-O character to these states along Γ-M. The feature along Γ-X (and Γ-Y) arises from the interior; the only likely candidate is Cu-O states.

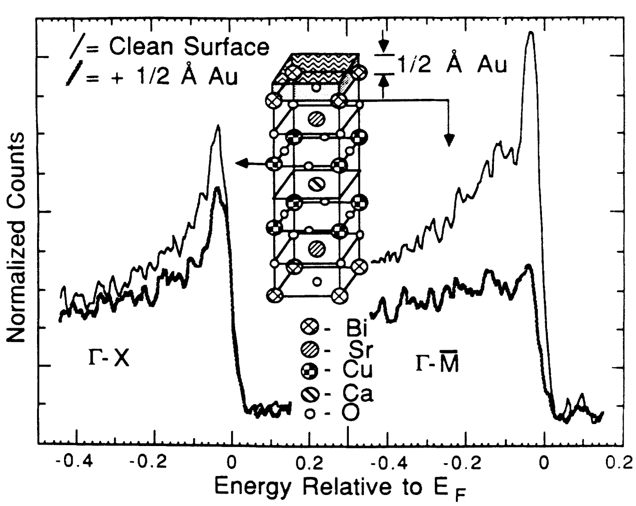

FIG. 2. Photoemission spectra of the states at the Fermi level along both the Γ-X and the Γ-M directions before and after deposition of $\frac{1}{2}$ Å of Au. Spectra were taken at 20 K with 19-eV photons and are normalized to incident photon flux. Inset: A schematic representation of the experiment. The actual Au overlayer is not continuous but consists mostly of isolated Au atoms. Arrows indicate the layers from which we believe each feature originates.

The presence of Fermi surface states near M is consistent with the LDA calculation. However, this region is complicated and the band in this region may not form an electron pocket as predicted by the LDA calculation. More complete band mapping is necessary to determine the exact nature of the states along Γ-M. Nevertheless, it is clear that there is a band crossing the Fermi level along Γ-M that has some Bi-O character and this is a different character from the band that crosses the Fermi energy in the Γ-X direction. The Fermi surface has sections with two distinct characters, one with Bi-O content and one without; that in itself is consistent with the LDA calculation.

Perhaps the most important conclusion from this experiment is that for the undisturbed material, the atomic surface is superconducting. Effects such as reduced coupling at the surface and the influence of the short coherence length are apparently not strong enough to quench the surface superconductivity. Because the finite resolution of our experiment, it is impossible to tell if the gap is complete or if there are still some states at the Fermi level. It is clear that we see evidence of an order parameter existing and at least a partial gap forming. The evidence indicates that the order parameter does continue up to

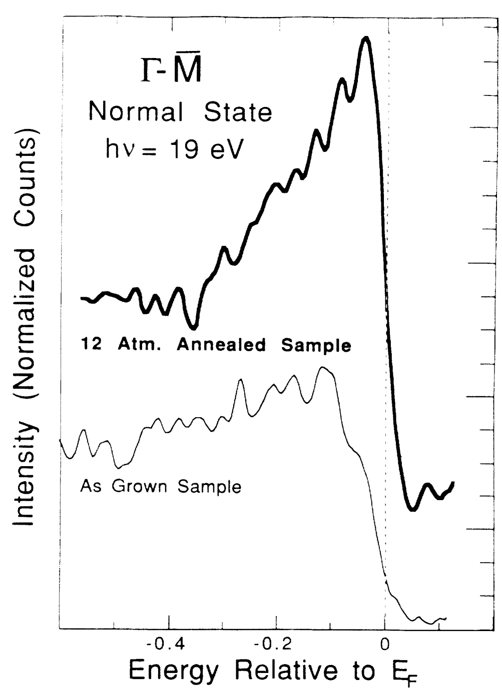

FIG. 3. Comparison of the feature nearest the Fermi level along the Γ-M direction between the as-grown sample and the 12-atm-O_2-annealed sample. Spectra are normalized to incident photon flux. There was little difference between the two samples in the spectra taken along the Γ-X direction. The spectrum for the 12-atm-O_2-annealed sample was taken at $T=90$ K, for the as-grown sample $T=100$ K.

the atomic surface. This result, however, is only true for a very clean, perfect surface. We know that the surface of the high-T_c materials is unstable in the presence of surface adatoms and disrupting processes such as sputtering. We expect that only carefully prepared surfaces held in vacuum will show superconductivity.

There were significant differences between the as-grown samples and the samples annealed in 12 atm of oxygen. The feature along the Γ-X direction appeared similar in all samples. However, along the Γ-M direction, the band with Bi-O character, there was a clear difference. Figure 3 shows the feature nearest to the Fermi level that we observed along the Γ-M direction for both the as-grown and the 12-atm-annealed sample. As mentioned before, there is a feature indicating states at the Fermi level for the 12-atm sample. For the as-grown sample, the only feature in this region is small, broad, and shifted away from the Fermi energy. This feature may be a second, deeper band. Regardless of the exact nature of this feature, it is well below the Fermi energy and there is no evidence for a band crossing the Fermi level along Γ-M in the as-grown sample. We do not yet know the reason for this change. It may be due to the change in oxygen content, the post-annealing treatment, or some other difference between the samples. Nevertheless, some 2:2:1:2 superconducting samples have a band crossing the Fermi level with Bi-O character while others do not. Apparently the metallic Bi-O states are not necessary for high-temperature superconductivity in this material and probably have no direct role in the pairing process. This result implies that the earlier STM data which suggest that the Bi-O layer is nonmetallic may be correct for the samples studied but is not generally true for the 2:2:1:2 material. Further information about the doping process will be published later.[23]

In summary, we have found metallic Cu-O bands in the 2:2:1:2 material for all the different oxygen doping levels studied. The Bi-O layer is also metallic for the $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductor which has been annealed in 12 atm of oxygen. A superconducting-gap feature is observed in all cases where there are states at the Fermi level. It is important to note that the atomic surface layer itself is superconducting in cases where the Bi-O layer is metallic. This is particularly important for a material with such a short coherence length. The presence of a superconducting surface may have implications to applications involving tunneling. Also, we have provided additional information about the character of the Fermi surface at different positions in the Brillouin zone, which is consistent with the Fermi surface predicted by LDA calculations. Any comprehensive theory of the normal state should account for this bandlike Fermi surface as well as nonbandlike features, such as strong correlation satellite structures, that have been observed in all of the photoemission work.

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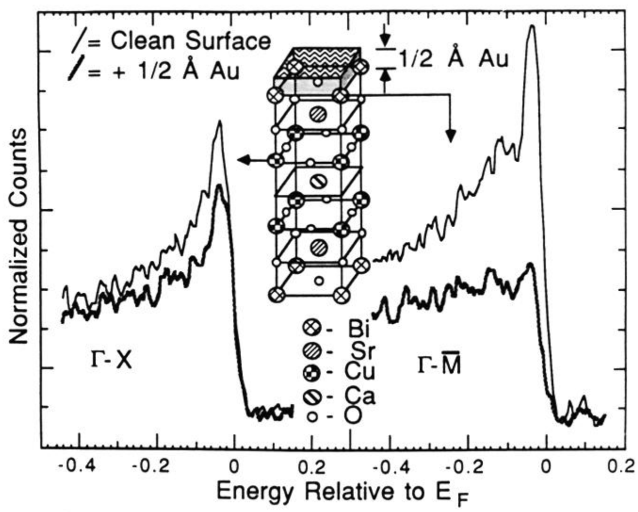

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