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DISCLAIMER

PHOTOEMMISSION AND ELECTRONIC STRUCTURE STUDIES OF $YBa_2Cu_3O_x$

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Abstract – High-resolution angle-resolved photoelectron spectroscopy measurements are reported for $YBa_2Cu_3O_x$ when the oxygen stoichiometry x is varied between 6.9 (92 K superconductor) and 6.2 (insulator). Fermi surfaces obtained from energy distribution curve measurements on a grid scanning the entire first Brillouin zone are reported for the x = 6.9 sample. Bands along the Γ-S symmetry line were measured for samples with reduced oxygen stoichiometry. For superconducting samples, these bands are essentially independent of x. As the material becomes insulating (x < 6.4), a dramatic falloff of spectral weight near E_F is observed. Resonant spectral features also disappear. Efforts to observe a superconducting gap are reported.

Keywords: photoemission, Fermi surface, electronic structure, oxygen stoichiometry

INTRODUCTION

In spite of intensive study, many fundamental properties of the high T_c oxide superconductors remain poorly understood. No general consensus has been reached to identify the excitation(s) that mediates electron pairing, nor even to clearly establish whether a strong or weak coupling formalism is most appropriate. Furthermore, a firm consensus has not been reached whether the normal state metallic behavior is best described as a Fermi liquid or if the essential physics is contained in a different description of the spin and charge states [1-5].

Within resolution limitations, recent angle resolved photoemission experiments provide support for a Fermi liquid picture. Spectral features, apparently resulting from bands dispersing in k-space, were followed across the Brillouin zone until they terminated at E_F. The apparent Fermi level band crossings were then mapped to measure the "Fermi surface". In general, these Fermi surface measurements [6-9] were in good agreement with the predictions of band theory [10, 11]. Positron annihilation measurements also provide strong support for the band theory predictions [12, 13].

Further, by monitoring electron states at the Fermi level using photoemission, the superconducting energy gap was observed in $Bi_2Sr_2CaCu_2O_8$ by several research groups [14-16]. Recent work [17] even shows evidence for gap anisotropy in this material, although earlier work did not [18].

While band theory has recorded many successes in the study of $YBa_2Cu_3O_x$ (Y123) with stoichiometry near x = 7, band theory fails for x = 6, where the material is insulating (band theory predicts metallic behavior [19]). It is recognized that electron correlation effects are sufficiently strong, for small x, so that the usual application of band theory becomes inappropriate. It is especially unclear how the intermediate stoichiometries should be described.

Consequently, in this paper, we report photoemission results from a study of Y123 when oxygen stoichiometries in the compound are varied. We give primary emphasis to a comparison of the

compositions x = 6.9 (T_c = 92 K) and x = 6.35; the latter is a non-superconductor with composition that is very close to the metal-insulator transition. We examine the variation, with x, of intense spectral features at E_F and at 1 eV binding energy. Efforts to observe a superconducting energy gap are discussed.

EXPERIMENTAL

Single crystals of Y123 with varied oxygen stoichiometries were prepared at Argonne National Laboratory. The oxygen stoichiometries were controlled by annealing the samples at 500°C in a flowing gas stream containing a predetermined mixture of O_2 and N_2, followed by a quench to liquid nitrogen. T_c's were determined by SQUID magnetization measurements. Transition widths vary between 0.2 and 3 K. The crystals with x = 6.35 do not show a superconducting signal above about 5 K. The crystals with x = 6.9 have a T_c of 92 K. All the measured crystals were twinned, therefore, Γ-X and Γ-Y are indistinguishable.

Three different photon sources were used for the photoelectron spectroscopy measurements: He I radiation ($h\upsilon$ = 21.2 eV), the Los Alamos ERG beamline at the National Synchrotron Light Source in Brookhaven National Lab, and the Ames/Montana ERG/Seya beamline at the Synchrotron Radiation Center at Stoughton, Wisconsin. For all three sources, photoelectrons were energy analyzed by a 50 mm radius hemispherical analyzer mounted on a goniometer; the analyzer has two degrees of rotational freedom. The angular resolution of the analyzer is 2°, which corresponds to k resolution of 0.073 $Å^{-1}$ (about 1/11 of the Γ to X(Y) distance in k-space) for 21.2 eV photons. The overall energy resolution (electron and photon) using a 2 eV pass energy is 30 meV at 21.2 eV photon energy. Samples were cleaved at 20 K in a vacuum better than 4×10^{-11} Torr. The position of the Fermi level was determined by measuring the Fermi edge of a clean Pt foil which was in electrical contact with the samples.

RESULTS AND DISCUSSION

Fermi surfaces

When oxygen is removed from Y123, that oxygen is removed from the Cu-O "chains". In oxygen deficient Y123, there is a strong tendency for oxygen vacancy ordered structures to form [20]. A dominant ordered form is the Ortho II structure, which consists of alternate rows of filled and empty (oxygen depleted) chains. According to deFontaine et al. [21], this ordered phase occurs over a substantial range of oxygen stoichiometry, including the x = 6.35 composition. This double-cell ordering is routinely observed in electron diffraction studies. Since the state of oxygen vacancy order in the basal plane has a profound effect on superconducting, structural and normal state electronic properties [22], a description of the electronic properties must include this ordering. For stoichiometries near x = 6.5, band calculations can be performed assuming ordering in the double cell Ortho II structure. We expect that, at x = 6.35, Y123 will exist in the Ortho II phase, although the phase must be highly defective. Since the predictions of band theory have served as an excellent guide to assist the experimentalists in interpreting photoemission data for oxygen rich Y123, we similarly analyze our photoemission data for the x = 6.35 sample with reference to the band theory predictions for the Ortho II phase [23]. For comparison, we present Fermi surface measurements for both x = 6.9 and 6.35 compositions.

The Fermi surfaces reported in Ref. 6 were obtained from ARPES measurements using 50 eV synchrotron radiation and a resolution capability of about 100 meV. Such resolution capability is less than desired for good definition of the Fermi surface. Consequently, we report, in Fig. 1, new measurements of the Fermi surface for $YBa_2Cu_3O_{6.9}$, from ARPES data taken at 21.2 eV, with the Ames-Montana facility, with spectral resolution of approximately 30 meV (with 2 eV pass energy) or 55 meV (with 5 eV pass energy). These data were taken on a grid of points in k-space separated by 2° in both θ and φ. The solid lines are Fermi surfaces calculated by Yu et al. [10]. Since the sample was twinned, the experimental data are expected to be symmetrical about the Γ– S line. Consequently, only the experimental points (open circles) left of or on the Γ-S line in Fig. 1 are marked.

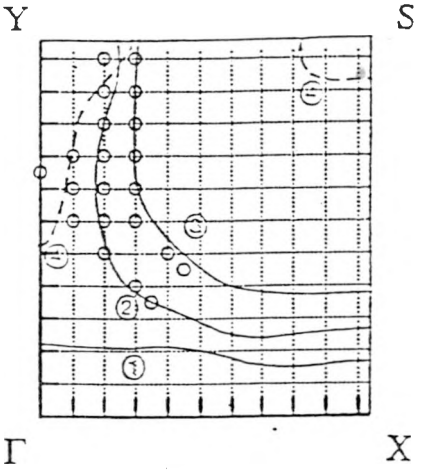


Fig. 1. Measurements (open circles) of the Fermi surface of $YBa_2Cu_3O_{6.9}$, compared to the calculated Fermi surface (solid lines) of Ref. 10.

The experimental Fermi surface of Fig. 1 was obtained from measurements such as those displayed in Fig. 2a. Here angle resolved energy distribution curves (EDCs) are presented for **k**-space points along the Γ- S line. The actual k-points where EDCs were taken are indicated by solid dots in the inset. We observe that, in progressing from Γ toward S, spectral features develop and shift toward E_F. An apparent Fermi surface crossing occurs when θ/ϕ are approximately 9/9. This crossing occurs near band (3) shown in the inset of Fig. 2a. A second feature, visible in Fig. 2a as a shoulder at about -0.1 eV for θ/ϕ = 4/4, also appears to grow in intensity and disperse toward E_F with increasing θ/ϕ until the feature passes through E_F at about θ/ϕ = 7/7. This feature forms the Fermi surface (2) labelled in Fig. 2a (inset).

Shown in Fig. 2b are EDCs for the x = 6.35 sample taken for nearly the same point grid along the Γ-S line as used for the x = 6.9 sample. The data of Fig. 2a and 2b look remarkably similar. Most obvious, in both compositions, is the abrupt drop in intensity near E_F at θ/ϕ = 9/9 or 10/10. These results suggest that Fermi surfaces exist in Y123 at (or very near) both stoichiometries and their Fermi surface dimensions (as probed along the Γ-S line) are essentially identical.

We know that correlation effects must be playing an important role in the x = 6.35 sample since it is nonmetallic below about 75 K where the resistivity begins to show a negative temperature dependence. If activated behavior is assumed, the measured R(T) suggests that a small gap (< 5 meV) has opened in the x = 6.35 sample. No effect of this gap was observed in the PES data. We have observed similar dispersive behavior at x = 6.4, 6.5 and 6.7. Thus we proceed to examine the data with reference to band theory.

Yu and Freeman [23] have calculated the band structure for the double cell structure appropriate for the fully ordered x = 6.5 composition. In the Γ-X direction, the Brillouin zone is truncated to half its former size. Except for the truncated zone and some modification in the shape of the Fermi surface in the vicinity of the new zone boundary, the Fermi surfaces for the double-cell structure are found to be essentially unchanged from those of the single-cell, x = 7 structure. Thus, the band theory results for the double-cell structure suggest that Fermi surface dimensions for the x = 6.35 sample, as probed along the 45° line ($\theta = \phi$), should be nearly identical to those obtained for the x = 6.9 stoichiometry. Dispersive properties of plane-related bands are predicted to be relatively unchanged as the stoichiometry is changed from x = 7 to 6.5. These predictions are clearly supported by the remarkable similarity of the EDCs displayed in Figs 2a and 2b.

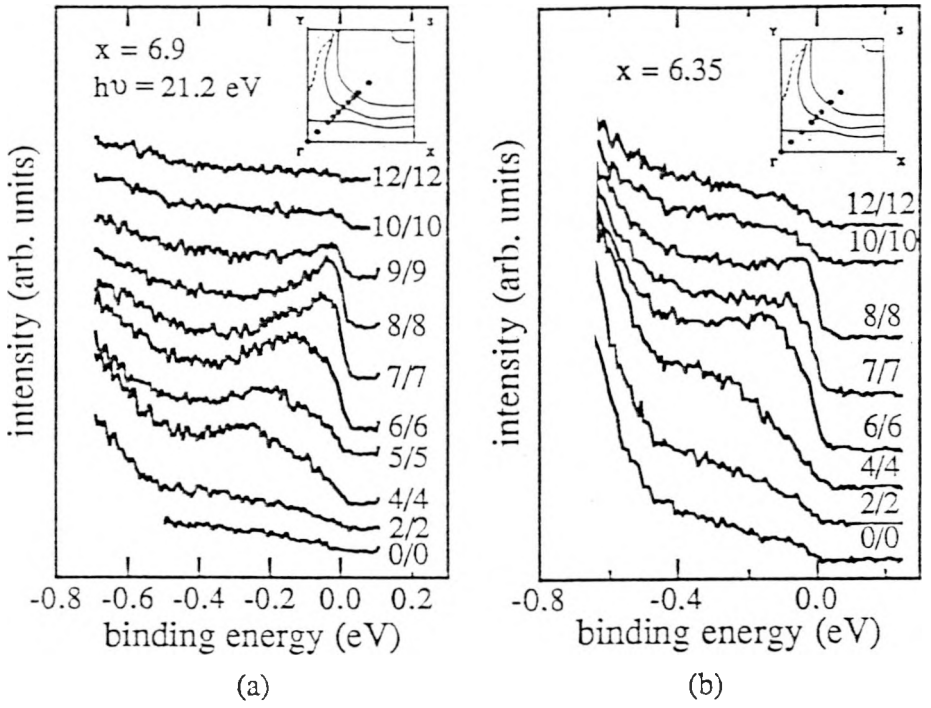


Fig. 2. Energy distribution curves (EDCs) for $YBa_2Cu_3O_x$ when (a) x = 6.9 and (b) x = 6.35, taken along the Γ-S symmetry line. The EDCs displayed correspond to k-points in the Brillouin zone indicated by dots in the insets. The spectra indicate that a dispersing band crosses E_F near θ/ϕ = 9/9 for both stoichiometries.

Spectral weight near E_F

Figure 3 shows EDCs within 2 eV below E_F for samples with three different oxygen stoichiometries. These spectra were taken at the same k-point (θ = ϕ = 6° with hυ = 21.2 eV) using the Ames-Montana facility at Stoughton, WI. The data were normalized at $E > E_F$, to the background signal that results from inelastic electrons excited, by second order light, from the valence band [24]. (In Fig. 3, this background has been subtracted.) We see that, for the compositions x = 6.9, 6.35 and 6.2, the spectral weight near E_F systematically falls. We have recently observed very little change in this spectral weight for the composition range $6.4 \leq x \leq 6.9$ where the material is superconducting.

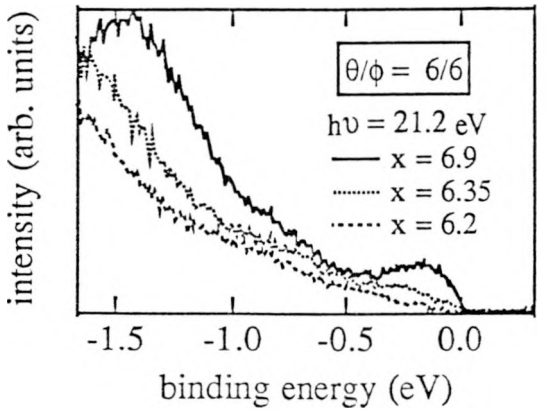


Fig. 3. EDCs measured with hυ = 21.2 eV, at a common k-point, for x = 6.9, 6.35, and 6.2. As oxygen stoichiometry x is reduced below 6.35, the intensity near E_F decreases.

In Fig. 4, EDCs are compared (normalized as before) for x = 6.9 and 6.35 for the line Γ-S. Again, spectral weight near E_F is consistently diminished for the oxygen depleted x = 6.35 sample. We have examined a grid of points throughout the Brillouin zone and consistently find attenuated spectral weight at E_F for the x = 6.35 stoichiometry when compared to x = 6.9. It would appear that, as the composition crosses the metal-insulator line, a rather abrupt change in spectral weight at E_F occurs signaling the breakdown of Fermi liquid theory and the inapplicability of band theory to describe the normal state electrons.

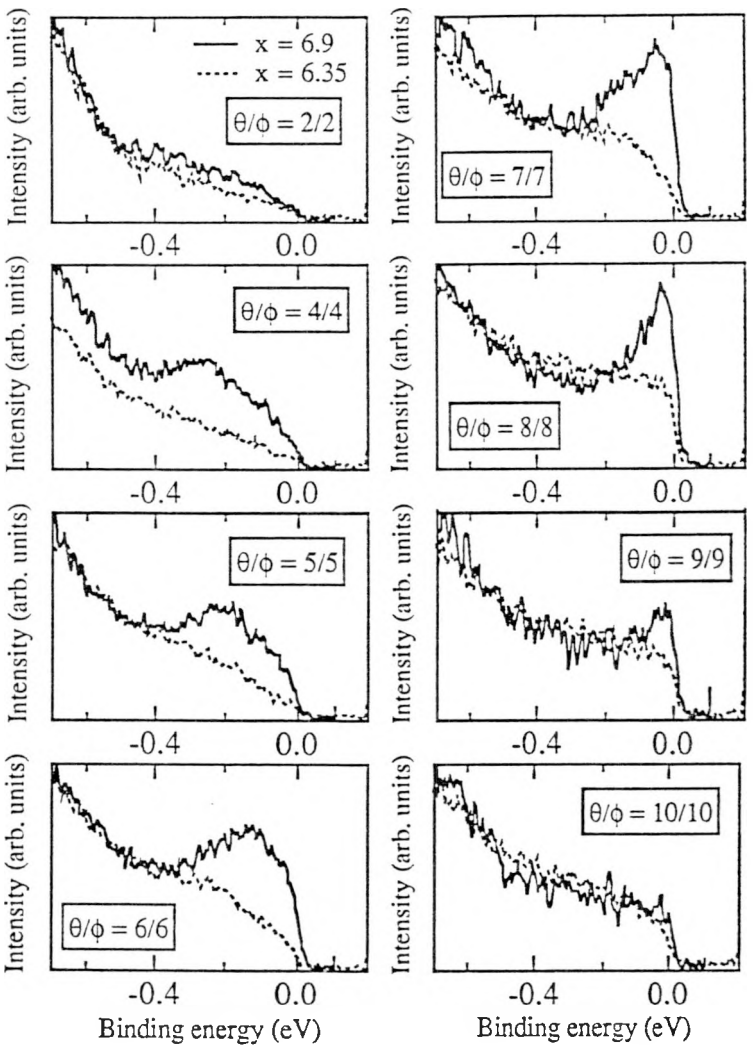


Fig. 4. EDCs measured with hυ = 21.2 eV, along the Γ-S line for x = 6.9 and 6.35. At all k-points, the spectral weight near E_F is diminished for the x = 6.35 sample.

Resonant features

There are a number of spectral features in the ARPES spectrum of Y123 that show a distinctly resonant character, i. e., photoemission intensities are very strong in specific k-regions and at specific energies of the photoexciting radiation. Of particular note are features that appear at E_F and at about 1 eV below E_F. The feature at E_F is very intense at hν = 17 eV in the vicinity of the Y point of the Brillouin zone [25]. Figure 5 (solid lines) shows EDCs for a x = 6.9 sample, for several points along the Γ-Y(X) line (this sample was twinned, so X and Y could not be distinguished). The feature at E_F is remarkably sharp. Since its width is essentially that of the instrument function, the intrinsic width could be significantly less than 30 meV. The fact that the feature is resonant at 17 eV suggests that the nature of normally empty states, approximately 17 eV above E_F controls this intensity.

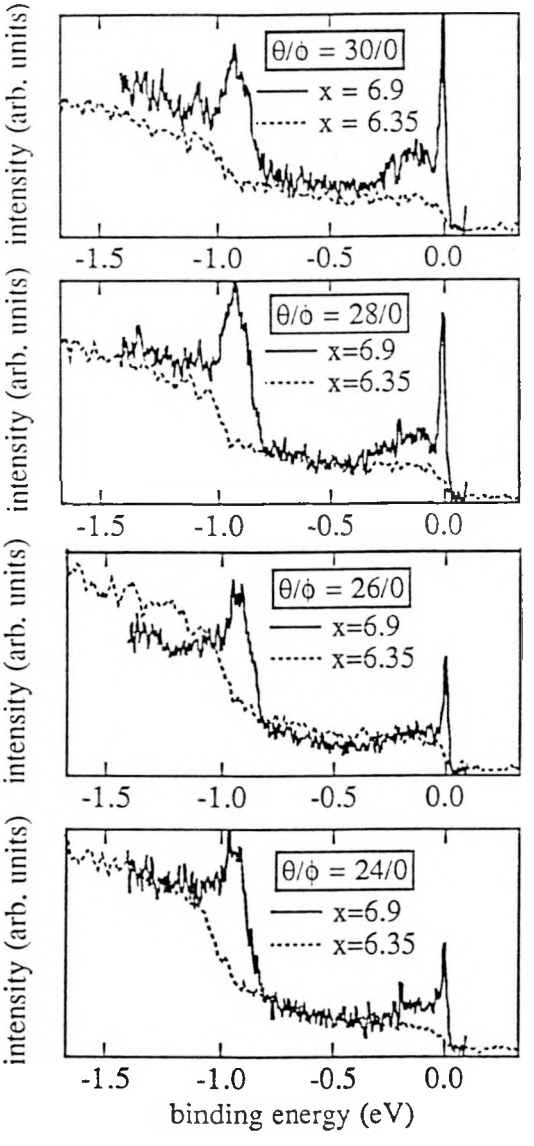


Fig. 5. EDCs measured with hυ = 17 eV, along the Γ-Y(X) line for x = 6.9 and 6.35. Intense spectral features at E_F and 1 eV binding energy, apparent at x = 6.9, disappear at x = 6.35.

Unless unusual relaxation processes are involved in the excitation, the sharp Fermi level feature indicates that a narrow distribution of electrons is available at E_F and that these electrons probably have a specific angular momentum character that enables them to couple with appropriate final states (reached with 17 eV radiation). Such Fermi level features may, of course, play an important role in forming the electron pairs that condense into the superconducting state. We note that, at x = 6.35, where the material is (marginally) no longer superconducting, the intense spectral feature has disappeared. The variation of this feature with oxygen stoichiometry (and T_c) is being systematically studied.

Another intense feature, near 1 eV binding energy, is apparent in Fig. 5 for the x = 6.9 sample. This feature also dramatically attenuates when the oxygen content is depleted to x = 6.35. Although the 1 eV feature is clearly apparent in Fig. 5, for x = 6.9, where the photon energy is 17 eV, the feature is much more intense at 24 eV [25]. Again, the sensitivity to photon energy suggests that the nature of the empty levels (into which electrons are excited), or Fano resonant enhancement by a coupled excitation, must play an important role. Figure 6 shows that the intensity of the 1 eV feature, measured with hυ = 24 eV, has fallen dramatically when x = 6.35 and disappears completely when x = 6.2.

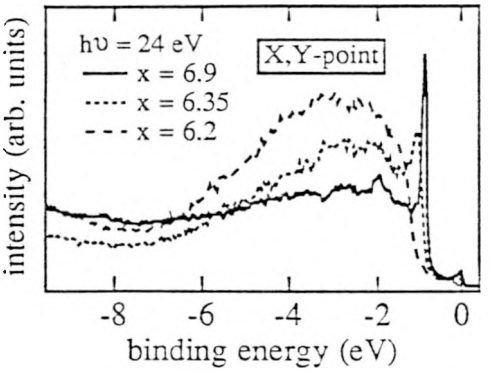


Fig. 6

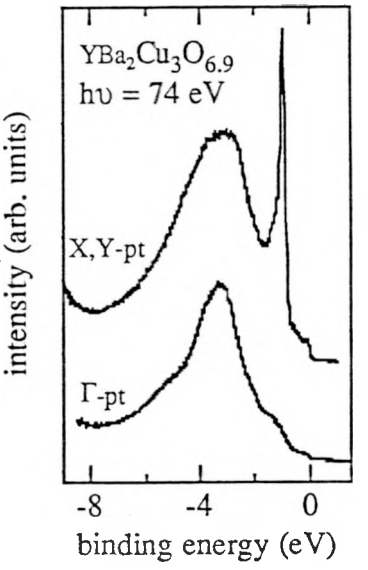
EDCs measured with hυ = 24 eV, at the Y(X) point for x = 6.9, 6.35, and 6.2.

Figure 7 shows angle resolved EDCs taken at the X-point and at the Γ-point when the photon energy is 74 eV. At this photon energy, the valence band Cu 3d electrons may show Fano resonant behavior. An additional excitation channel involving Cu 3p to Cu 3d electrons becomes allowed. For Cu compounds, the 74 eV Fano resonant behavior is normally associated with the valence band satellites [26]. However, the 1 eV feature, at the X (and Y) points, apparently shows Fano resonance behavior at 74 eV. The data in Fig. 7 are on-resonance. This behavior indicates that the 1 eV feature must have substantial Cu 3d angular momentum character in the vicinity of the X and Y points.

We have examined this feature in both the Γ-X and Γ-Y directions in studies of detwinned crystals. No clear difference was observed in the spectra for these directions. Consequently, it seems unlikely that the feature is associated with chains since their bonding is highly asymmetrical in the a and b directions. We cannot convincingly demonstrate that the feature is (is not) a surface state [25, 27]. However, if it represents a bulk state, then the feature must be associated with the planes where the anisotropy is small.

Fig. 7.

EDCs for $YBa_2Cu_3O_{6.9}$ measured with hυ = 74 eV, at the Γ-point and the Y(X)-point. The feature at 1 eV binding energy at Y(X)-point is very intense at hυ = 74 eV, indicating Fano resonant behavior.



Energy gap

An important accomplishment for ARPES has been the successful observation and measurement of the superconducting gap in $Bi_2Sr_2CaCu_2O_8$ compounds [14-18]. However, the gap has not been observed in Y123. In Fig. 8 we show an attempt to measure the gap in $YBa_2Cu_3O_{6.9}$, using high resolution ARPES data taken at 21.2 eV photon energy using He I radiation. In Fig. 8a, we show spectra, at T = 90 K, for Y123 and for silver (a Fermi edge reference) that is in electrical contact with the Y123 sample. The Y123 data are recorded at a k-point where the band along Γ-S crosses the Fermi level.

Both the superconductor, in its normal state, and the silver provide equivalent, precise determinations of the Fermi edge. In Fig. 8b, similar data, taken when T was approximately 20 K, are presented. Both silver and Y123 show a sharper edge, a consequence of reduced thermal smearing. However, there is no indication of a superconducting gap. Similar results were obtained on measurements of three different samples.

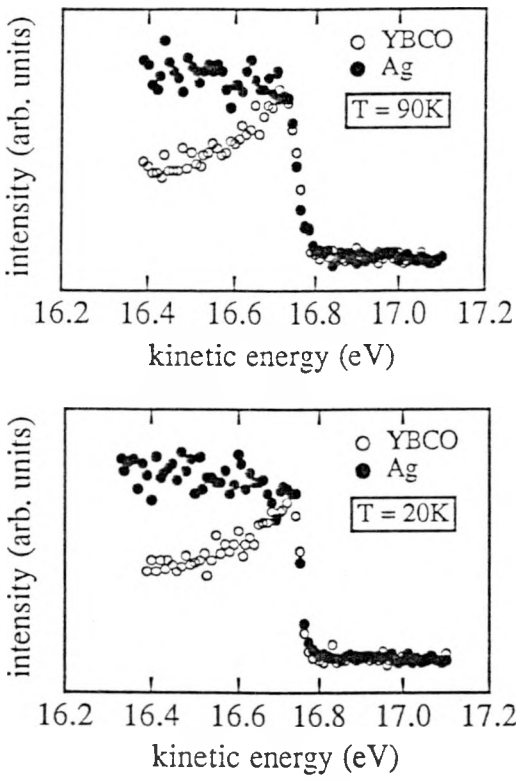


Fig. 8. An attempt to observe the superconducting gap in $YBa_2Cu_3O_{6.9}$. EDCs near E_F for $YBa_2Cu_3O_{6.9}$ are compared to measurements for Ag which has a well defined Fermi edge. No indication of a superconducting gap is observed.

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REFERENCES

1. Lee Patrick A., *Phys. Rev. Lett.* **63**, 680 (1989); Nagaosa Naoto and Lee Patrick A., *Phys. Rev. Lett.* **64**, 2450 (1990).
2. Kampf A. P. and Schrieffer J. R., *Phys. Rev. B* **42**, 7967 (1990).
3. Anderson P. W., *Science* **235**, 1196 (1987); *Phys. Rev. B* **42**, 2624 (1990).
4. Varma C. M., Littlewood P. B., Schmitt-Rink S., Abrahams E. and Ruckenstein A. E., *Phys. Rev. Lett.* **63**, 1996 (1989).
5. Kim Ju H., Levin K. and Auerbach A., *Phys. Rev. B* **39**, 11633 (1989).
6. Campuzano J. C., Jennings G., Faiz M., Beaulaigue L., Veal B. W., Liu J. Z., Paulikas A. P., Vandervoort K., Claus H., List R. S., Arko A. J. and Bartlett R. J., *Phys. Rev. Lett.* **64**, 2308 (1990).
7. Olson C. G., Liu R., Lynch D. W., List R. S., Arko A. J., Veal B. W., Chang Y. C., Jiang P. Z. and Paulikas A. P., *Phys. Rev. B* **42**, 381 (1990).
8. Takahashi T., Matsuyama H., Katayama-Yoshida H., Okabe Y., Hosoya S., Seki K., Fujimoto H., Sato M. and Inokuchi H., *Phys. Rev. B* 39, 6636 (1989).
9. Mante G., Claessen R., Buslaps T., Harm S., Manzke R., Skibowski M. and Fink J., *Z. Phys. B* **80**, 181 (1990).
10. Yu J., Massidda S., Freeman A. J. and Koelling D. D., *Phys. Lett. A* **122**, 203 (1987).
11. Krakauer H. and Pickett E., *Phys. Rev. Lett.* **60**, 1665 (1988); Pickett W. E., Cohen R. E. and Krakauer H., *Phys. Rev. B* **42**, 8764 (1990).
12. Smedskjaer L. C., Liu J. Z., Benedek R., Legnini D. G., Lam D. J., Stahulak M. D., Claus H. and Bansil A., *Physica* (Amsterdam) **156C**, 269 (1988) and this conference.
13. Lynn K. G. et al., this conference.
14. Imer J.-M., Pathey F., Dardel B., Schneider W.-D., Baer Y., Petroff Y. and Zettl A., *Phys. Rev. Lett.* **62**, 336 (1989).
15. Manzke R., Buslaps T., Claessen R. and Fink J., *Europhys. Lett.* **9**, 477 (1989).
16. Olson C. G., Liu R., Yang A.-B., Lynch D. W., Arko A. J., List R. S., Veal B. W., Chang Y. C., Jiang P. Z. and Paulikas A. P., *Science* **245**, 731 (1989).
17. Shen Z. X. et al., this conference.
18. Olson C. G., Liu R., Lynch D. W., List R. S., Arko A. J., Veal B. W., Chang Y. C., Jiang P. Z. and Paulikas A. P., *Solid State Commun.* **76**, 411 (1990).
19. Herman Frank , Kasowski Robert V. and Hsu William Y., *Phys. Rev. B* **36**, 6904 (1987); Fujiwara T. and Hatsugai Y., *Jpn. J. Appl. Phys.* **26**, L716 (1987).
20. Reyes-Gasga J., Krekels T., Van Tenderloo G., Van Landuyt J., Amelincks S., Bruggink W. H. M. and Verweij H., *Physica C* **159**, 831 (1989); Hervieu M., Domenges B., Raveau B., Post M., McKinnon W. R. and Tarascon J. M., *Materials Letters* **8**, 73 (1989).
21. deFontaine D., Ceder G. and Asta M., *J. Less Common Metals* **164&165**, 108 (1990); *Nature* **343**, 544 (1990).
22. Veal B. W., Paulikas A. P., You H., Shi H., Fang Y. and Downey J. W., *Phys. Rev B* **42**, 6305, 4770 (1990); Jorgensen J. D., Pei S., Lightfoot P., Shi H., Paulikas A. P. and Veal B. W., *Physica C* **167**, 571 (1990); Claus H., Yang S., Paulikas A. P., Downey J. W. and Veal B. W., *Physica C* **171**, 205 (1990).
23. Yu J. J. and Freeman A. J., unpublished.
24. Allen J. W., Olson C. G., Maple M. B., Kang J.-S., Liu L. Z., Park J.-H., Anderson R. O., Ellis W. P., Markert J. T., Dalichaouch Y. and Liu R., *Phys. Rev. Lett.* **64**, 595 (1990).
25. Olson C. G. et al., this conference.
26. Shen Z. X., Allen J. W., Yeh J. J., Kang J.-S., Ellis W., Spicer W., Lindau I., Maple M. B., Dalichaouch Y. D., Torikachvili M. S., Sun J. Z. and Geballe T. H., *Phys. Rev. B* **36**, 8414 (1987); Ghijsen J., Tjeng L. H., Eskes H., Sawatzky G. A. and Johnson R. L., *Phys. Rev. B* **42**, 2268 (1990).
27. Claessen R., Mante G., Hub A., Manzke R., Skibowski M., Wolf T. and Fink J., to be publishd.