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Photoemission study of the new high-temperature superconductor Bi-Ca-Sr-Cu-O

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We present the first photoemission data on the recently discovered family of high-temperature superconductors that do not include rare earths. Synchrotron-radiation photoemission spectra were taken both on sintered and on cleaved single-crystal specimens of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$. Both samples were single phase and had sharp superconducting transitions at 85 K. The differences and similarities with respect to $YBa_2Cu_3O_{7-x}$ are discussed, and the data are compared to the results of one-electron density-of-states calculations.

High-temperature superconductivity, an already extremely productive area of research, has recently produced a new stream of exciting results.[1-4] A new family of Bi-based materials was discovered and confirmed, with critical temperatures up to 107 K. We present the first experimental study of the electronic structure on the 85-K superconducting phase, since we were able to prepare this compound as a single phase. The study was performed on sintered and single-crystal specimens of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ (Bi-Ca-Sr-Cu-O), using synchrotron-radiation photoemission spectroscopy. The results show that, contrary to $YBa_2Cu_3O_{7-x}$ and other 1:2:3 materials,[5,6] this compound exhibits a clear photoemission intensity edge at the Fermi energy E_F. The calculated one-electron density of states[7] qualitatively reproduces the observed spectral features, but the energy positions appear shifted by approximately 1.5 eV to lower energies. The spectra also exhibit a feature below the main valence bands which does not appear in the theoretical electronic structure but which may correspond to the peak observed ~9.5 eV below E_F in the 1:2:3 materials.[8]

Since the discovery of high-temperature superconductivity, photoemission spectroscopy has been very helpful in identifying the electronic structure of the new materials, and in studying its relation to the superconducting mechanism.[5,6] For some time, the use of sintered specimens cast serious doubts on the validity of the photoemission spectra, due to their high surface sensitivity. These questions were answered by spectra obtained on the cleaved surfaces of single-crystal $YBa_2Cu_3O_{7-x}$.[9] This stimulated us to use this probe in the study of the new superconductors in the Bi-Ca-Sr-Cu-O family. In order to avoid questions about the quality of the data, we performed experiments both on sintered specimens and on single-crystal specimens. The results are generally consistent with each other, although the relative intensities of some core-level peaks are different.

The growth of these samples has been described in detail elsewhere.[4] Both the sintered specimens and the single-crystal specimens were single phases, with a sharp superconducting transition at 85 K, measured resistively and magnetically, as shown in Fig. 1. The sintered samples were cleaned under ultrahigh vacuum conditions (2×10^{-19} Torr) by scraping with a diamond grinder. Extensive investigations have demonstrated that this is the most effective technique for preparing clean surfaces from sintered 1:2:3 materials. The single crystals were cleaved under vacuum using a technique similar to that described in Ref. 9. Because these crystals are soft and similar to mica, this method does not result in low-energy electron diffraction (LEED) patterns of quality comparable to

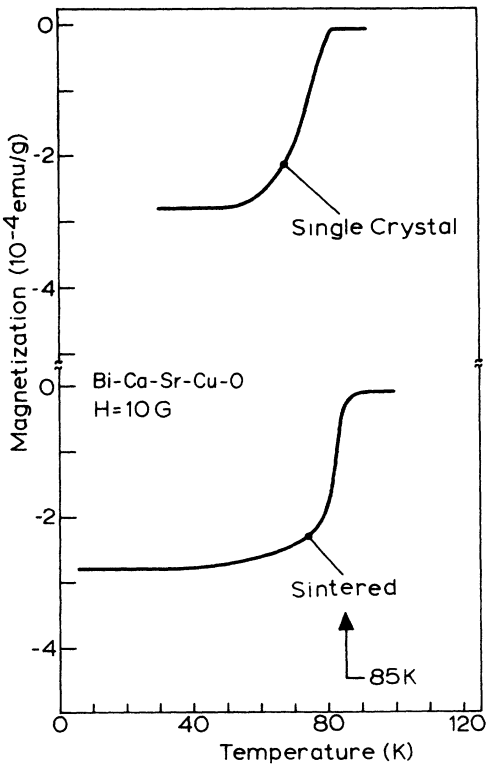

FIG. 1. Magnetization curves for single-crystal and sintered Bi-Ca-Sr-Cu-O as a function of temperature, obtained by cooling in a field of 10 G. The top curve has been arbitrarily normalized to the bottom curve, since the absolute magnetization of the irregularly shaped single crystal was not determined.

those obtained from single-crystal $YBa_2Cu_3O_{7-x}$.

Photoemission spectra were taken with an angle-resolved microscience electron energy analyzer. The photons were obtained by filtering the radiation emitted by the 1-GeV storage ring of the Wisconsin Synchrotron Radiation Center with a vertical Seya-Namioka monochromator. The experiments were performed at different photon energies in the range 15–40 eV. All results presented in this paper were consistently obtained on several surfaces obtained by scraping ceramic samples or by cleaving single crystals. We monitored the spectra for indications of contamination features arising from residual gas adsorption. Such symptoms were indeed observed starting approximately 30 h after the production of a clean surface, both for sintered and single-crystal specimens. The spectra discussed in this article were taken at much earlier times.

Figure 2 shows spectra obtained on a sintered Bi-Ca-Sr-Cu-O sample for energies in the upper part of the range used here. These spectra exhibit several core-level peaks, ~26, 23.4, and 17.7 eV below E_F. The first peak is due to the Bi $5d_{5/2}$ level, and the second is due to the Ca $3p$ level.[10] The third peak appears related to the Sr $4p$ levels, although the binding energy is significantly different with respect to that of metallic Sr.[10] We also see two shallower features, centered around 10–11 eV and ~4 eV below E_F. The last feature is due to valence states, mostly derived from Cu and O. The feature 10–11 eV below E_F is not predicted by one-electron theory, and may correspond to a peak observed ~9.5 eV below E_F for $YBa_2Cu_3O_{7-x}$ and other 1:2:3 materials.[5,6,9]

Figure 3 shows photoemission spectra taken at different photon energies on a single-crystal specimen of Bi-Ca-Sr-Cu-O. These spectra exhibit the same two main features in the energy range 0–11 eV below E_F, but show more detailed structure than was apparent for the sintered specimens. A careful study of the spectra at different photon energies reveals that the upper peak actually has four different features, 1.6, 3.4, 5.0, and 5.9 eV below E_F For comparison, the spectra taken on 1:2:3 materials exhibit only two features in this binding-energy region, ~2.5 and ~5.0 eV below E_F. Note, in particular, that the first feature of Bi-Ca-Sr-Cu-O is much closer to the Fermi level than that of the 1:2:3 samples.[5,6,9] Figure 4 shows a detailed comparison of Bi-Ca-Sr-Cu-O and $YBa_2Cu_3O_{7-x}$ spectra taken at the same photon energy.

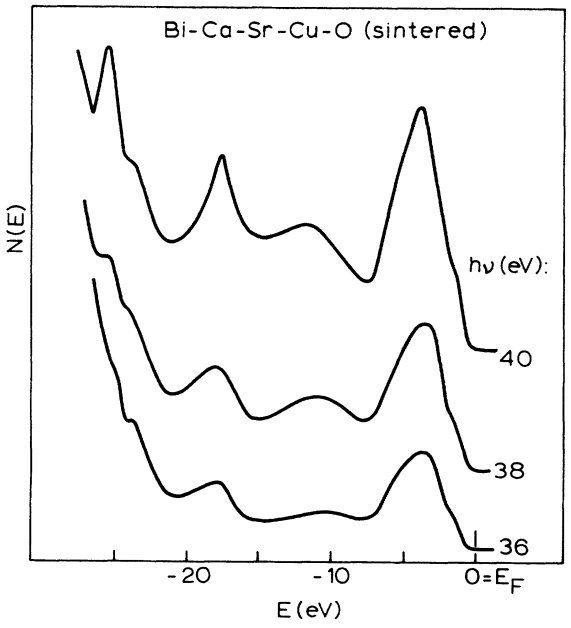

FIG. 2. Photoemission spectra taken at 36-, 38-, and 40-eV photon energy on a sintered Bi-Ca-Sr-Cu-O specimen, cleaned by scraping under vacuum.

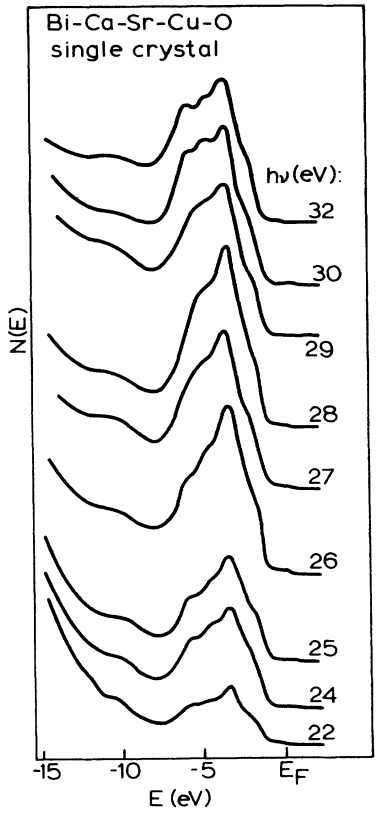

FIG. 3. Photoemission spectra taken at different photon energies on single-crystal Bi-Ca-Sr-Cu-O. The angle-resolved electron energy analyzer was placed in a direction near the sample normal.

We are aware of three one-electron calculations of the electron structure of Bi-Ca-Sr-Cu-O.[7,11,12] Figure 4 also shows a comparison between our spectrum and the calculated density of states by Massidda, Yu, and Freeman.[7] Note that, in order to optimize the resemblance between the two curves, the theoretical density of states was rigidly shifted by 1.7 eV towards higher binding energies. After this shift, the correspondence between theory and experiment is reasonable. The main peaks are primarily due to Cu-O hybridized states, but the theory also suggests that there are metallic bands composed of Bi $6p$ orbitals, some of which cross the Fermi energy.

One interesting feature which distinguishes the photoelectron spectra of Bi-Ca-Sr-Cu-O from the other oxide superconductors is the intensity of the signal near the Fermi level. From Figs. 2, 3, and 4, we see that the signal is less than 3% of the peak valence-band signal, and certain-

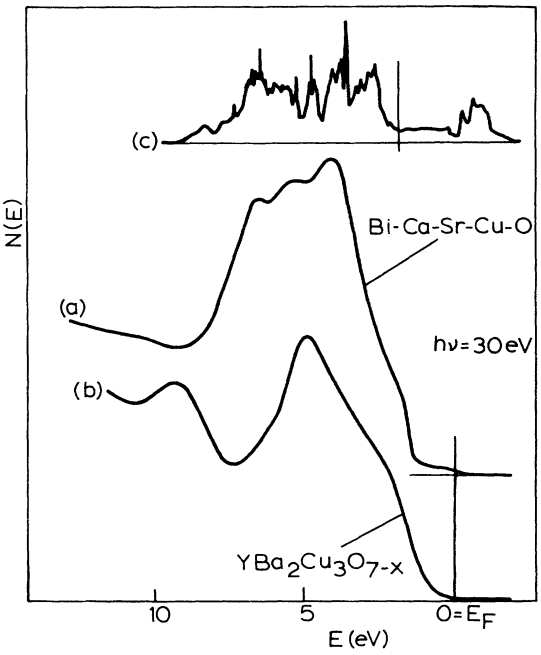

FIG. 4. (a) and (b) direct comparison between the spectra taken at 30-eV photon energy, close to normal emission, for single-crystal Bi-Ca-Sr-Cu-O (a) and single crystal $YBa_2Cu_3O_{7-x}$ (b). (c) Theoretical density of states from Ref. 7. The latter curve was rigidly shifted by 1.5 eV towards higher binding energy, in order to improve the correspondence with the experimental spectra.

ly weaker than in the theoretical density of states.[7] However, we did observe a clear Fermi edge. This is visible in the spectrum shown in Fig. 5. In order to show that the Fermi edge was not due to small metal inclusions, we studied the Fermi energy region very carefully for several surfaces obtained from different sintered specimens, and for several cleaved single crystals. Spectra exhibiting Fermi edges were produced by each of these surfaces. Therefore, we submit that the Fermi edge is not an artifact of some impurity phase, but an intrinsic feature of Bi-Ca-Sr-Cu-O. This is of course a very important fact, because the states at the Fermi level are central to the superconductivity. This result also shows that not all of the electronic states are shifted to higher binding energies by

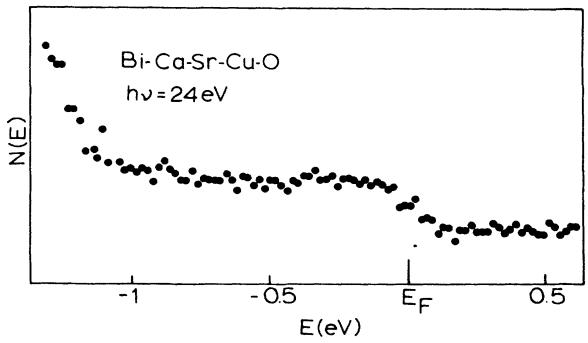

FIG. 5. Spectrum taken close to normal emission for single-crystal Bi-Ca-Sr-Cu-O at 24 eV photon energy, showing a clear Fermi edge.

correlation effects. We note that signal near E_F was also observed for certain photon energies and electron collection angles in the case of cleaved $YBa_2Cu_3O_{7-x}$.[9] However, a clear Fermi edge was never observed. Surprisingly, it was found by magnetic measurements that the Pauli paramagnetic susceptibility χ_p, which is proportional to the density of states at the Fermi level, is two times smaller for Bi-Ca-Sr-Cu-O than for $YBa_2Cu_3O_{7-x}$.

The nature of the −9.5-eV peak observed for 1:2:3 materials, generated considerable controversy.[8] Due to the coincidental appearance of features at similar energies on contaminated surfaces, several authors attributed the −9.5-eV peak to contamination. However, we presented evidence that the feature is intrinsic and related to oxygen.[8] The most likely explanation is a two-hole satellite of the oxygen-related features in the upper valence bands. We tentatively attribute the Bi-Ca-Sr-Cu-O peak centered at −10.2 eV in Figs. 2–4 to the same cause. Note, however, that the intensity of this peak relative to the main valence-band feature is markedly reduced with respect to the $YBa_2Cu_3O_{7-x}$ spectra.[8] This is consistent with the fact that the Bi-Ca-Sr-Cu-O structure does not require as many holes on the Cu-O planes as the 1:2:3 structure.

A preliminary search was performed for changes in the spectra when the temperature was lowered below the value corresponding to the onset of superconductivity. Although small changes cannot be excluded at this time, we rule out large modifications of the electronic structure near the Fermi edge. This indicates that, as in 1:2:3 compounds, the ratio between the superconductivity gap and the critical temperature is not anomalously high with respect to mean-field values, as was suggested by some of the early theoretical models of high-temperature superconductivity. We also note that our study of cleaved single crystal $YBa_2Cu_3O_{7-x}$ did not confirm the large temperature effects that had been previously reported by some authors for sintered 1:2:3 compounds.

Experiments are in progress to extend our study of the electronic structure of Bi-Ca-Sr-Cu-O and of other compounds in this novel family. The experiments are investigating, in particular, photoemission resonances occurring in the photon energy range above that explored in this work.[5,6] The present data, however, already provide a good picture of the valence electronic structure of Bi-Ca-Sr-Cu-O, of its similarity with respect to 1:2:3 materials, and of the strong points and limitations of the one-electron theoretical calculations.

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