High-Resolution Photoemission Study of the Low-Energy Excitations Reflecting the Superconducting State of Bi-Sr-Ca-Cu-O Single Crystals

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uv-photoemission spectra ($h\nu=21.2$ eV) of single-crystal specimens of the high-T_c superconductor $Bi_2Sr_2CaCu_2O_8$ have been measured with a resolution of 20 meV in the normal state at 105 K and in the superconducting state at 15 K. In a narrow energy range of 120 meV below the Fermi energy, the low-temperature spectra reveal unambiguously the low-lying quasiparticle excitations reflecting the superconducting state. A straightforward analysis of these spectra provides strong evidence for the existence of a superconducting gap with a reduced value $2\Delta/k_BT_c\simeq 8$.

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The recent discovery of high-T_c superconductors in a class of materials which are not far from the insulating state is at the origin of the sudden revival of this field.[1] In a very short period of time, new compounds have been discovered and important progress has been made in the preparation of monocrystalline samples of well-defined structure and stoichiometry. It would seem that their macroscopic bulk properties are now rather well established. On the other hand, the microscopic description of the basic mechanism responsible for the occurrence of high-temperature superconductivity is not settled and contradictory models are presented in the literature.[2] This confusing situation arises from the lack of consensus on the experimental data yielding a direct description of the microscopic phenomena taking place at the energy scale characteristic for superconductivity.

One of the most fundamental pieces of information which could allow one to test the validity of the assumptions underlying the different models is the spectrum of the low-energy excitations reflecting the superconducting state. From the analysis of numerous optical-spectroscopy[3] and electron-tunneling[3,4] data the existence of a superconducting gap was inferred and values of $2\Delta/k_BT_c$ ranging from 2 to 18 have been proposed in La-Sr-Cu-O and Y-Ba-Cu-O systems. Until now photoemission studies of the relevant narrow energy range below E_F have not yielded conclusive results. At $T>T_c$ the Fermi edge is at best barely discernible in Y-Ba-Cu-O systems,[5,6] whereas it can be clearly observed in Bi-Ca-Sr-Cu-O systems.[7-9] Upon cooling, both compounds show only extremely weak modifications[5,6] or in one case[10] a rather large variation considered by the authors to be consistent with the opening of a gap (see below). In this Letter we present and discuss high-resolution photoemission spectra of Bi-Sr-Ca-Cu-O monocrystals reflecting the typical low-energy excitations originating unambiguously from the superconducting state.

The crystals of $Bi_2Sr_2CaCu_2O_8$ were grown from a mixture of Bi_2O_3, CuO, $SrCO_3$, and $CaCO_3$ with molar percentages of 22.4%, 32%, 26.9%, and 18.7%, respectively. The powders were mixed in a ball mill with acetone, then placed in a gold crucible and heated at 920 °C for 5 h and cooled to 820 °C at a rate of 3 °C/h in flowing oxygen. The result was a black, glassy mass that cleaved into micaceous sheets. X-ray analysis showed that the c axis was perpendicular to the cleavage plane and had a spacing of 3.0 nm in agreement with the $Bi_2Sr_2CaCu_2O_8$ compound identified by Subramanian *et al.*[11] The stoichiometry was confirmed by scanning-electron-microscopy elemental analysis of single crystals from the same preparation batch. The samples were characterized by both four-probe dc resistance and dc magnetic susceptibility measurements, which indicated a bulk transition temperature of approximately 88 K. Full resistive transition widths were of order 2–3 K.

The relatively large samples, showing well oriented regions with glossy surfaces, were fixed with a conducting epoxy resin to a copper plate in good thermal contact with the cold finger of a closed-cycle He refrigerator. The temperature was measured with a Rh-Fe resistor attached to the copper support below the sample. From the lowest sample temperature at 15 K which could be achieved, a heating element allowed us to reach continuously higher temperatures up to 400 K. The photoemission measurements were performed in a spectrometer equipped with a commercial gas-discharge lamp producing the very narrow He I and He II resonance lines at 21.2 and 40.8 eV. The base pressure in the system was 3×10^{-11} Torr and rose to 3×10^{-10} Torr during the measurements with the discharge lamp. We have measured two samples from different batches. The first sample (S1) consisted of many sizable monocrystals with different orientations so that we cleaned its surface *in situ* with a tungsten brush. The second sample (S2) was a monocrystal with a large surface perpendicular to the c axis. In this case we could peel off extremely thin layers by gently rubbing the surface with the sharp edge of a blade oriented perpendicular to the surface. This produced perfectly glossy surfaces so that we believe it to be rather equivalent to a cleaving. Both procedures erode the sample rather slowly and could be repeated many times. During the measurements we created a fresh surface every 20 min in order to get rid of the adsorbates and to avoid important changes of the oxygen concentration in the Cu-O planes near the surface. Otherwise, during the 3 h necessary to accumulate a high-resolution spectrum with sufficient statistics, the characteristic feature attributed to the superconducting state is no longer observed. The position of the Fermi level used as the energy reference in all spectra was determined with an accuracy of ± 2 meV in each run by measurement of the Fermi edge of the copper plate on which the sample is fixed in good thermal and electrical contact. From this calibration at 15 K we also found that our total instrumental resolution was 20 meV. The intensity of the spectra presented below is given in arbitrary units, the maximum of the signal in the narrow-range spectra is about 4×10^3 counts and only a constant background has been subtracted from the rough data.

We are aware that a discussion of photoemission spectra in terms of density of states, apart from cross-section effects, is no longer straightforward when correlation among the band electrons is large, as is likely the case in this class of oxides. Furthermore, the low angular acceptance of our analyzer limits the sampling of the Brillouin zone. (However, the two different samples yield the same results.) Without underestimating the possible importance of these facts, we shall tentatively ignore them in the discussion of our spectra. We believe that they do not invalidate the relevance of the observed temperature effects.

Spectra taken with the He II line (40.8 eV) at 105 and 15 K in an energy range of 12 eV below the Fermi energy are in overall agreement with published data.[7-9] A representative spectrum of our measurements on sample S2 is shown in Fig. 1. We observed, however, that the spectra recorded under different conditions (samples, preparation, temperature, integration time) are not reproducible in the range between 5 and 12 eV. We intend to investigate specifically this effect since it may contribute to the characterization of the relation between the oxygen stoichiometry and the superconducting properties.[12,13] The main point of interest in the present study is, however, the observation of a well-defined Fermi edge, which we will concentrate on in the following.

In. Fig. 2 we present high-resolution photoemission

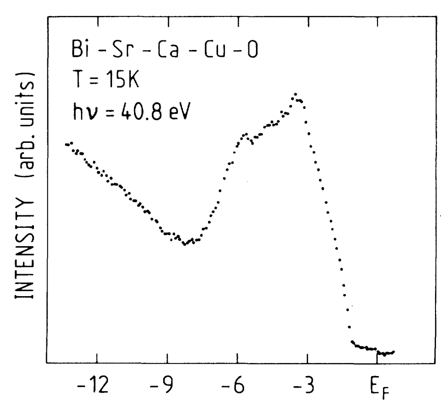

FIG. 1. Photoemission spectrum of Bi-Sr-Ca-Cu-O sample S2 in a wide energy range 12 eV below E_F.

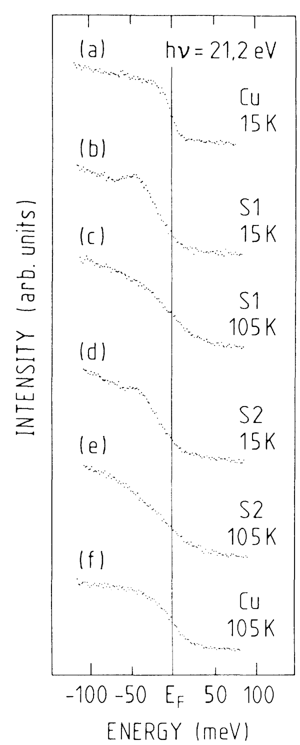

FIG. 2. Photoemission spectra of Bi-Sr-Ca-Cu-O samples (S1,S2) in the normal state [(c) and (e)] and the superconducting state [(b) and (d)]. Reference spectra of Cu [(a) and (f)] recorded under identical conditions. Note that the 200-meV energy range of these spectra corresponds to two data points around E_F in the wide energy range spectrum of Fig. 1.

spectra taken at $h\nu=21.2$ eV for the samples S1 [Figs. 2(b) and 2(c)] and S2 [Figs. 2(d) and 2(e)] in a narrow energy range of 120 meV below E_F. The spectra are obtained at the sample temperatures of 15 and 105 K which are, respectively, far below and markedly above $T_c=88$ K. Figures 2(a) and 2(c) show also, as a reference, the Cu Fermi edge recorded under identical experimental conditions. The most striking feature in this figure is the appearance of a peak at about 30 meV below E_F in the superconducting phase of both samples. Its amplitude is slightly lower in sample S2 than in sample S1 but its position is the same within the experimental uncertainty. This peak observed at low temperature might be simply due to an inherent structure of the density of states. We can rule out this possibility since by multiplying the low-temperature spectrum [Figs. 2(b) and 2(d)] with a Fermi function for $T=105$ K, this peak is only weakly attenuated, in contrast with the spectrum at 105 K [Figs. 2(c) and 2(e)]. In fact, since this peak has disappeared at 105 K, its presence at temperatures below $T_c=88$ K can be associated unambiguously with the concomitant change of the electronic structure upon the superconducting phase transition.

Many microscopic mechanisms have been proposed for the explanation of the new high-T_c superconductivity but at the present time, as far as we are informed, the only tractable prediction of the density of states in superconductors is still given by the Bardeen-Cooper-Schrieffer (BCS) model. This density of states is characterized by the opening around E_F of a gap 2Δ bordered by two peaks falling off very rapidly to the normal density of states. An useful aspect for the comparison with experiment is that the number of new states created below the gap in the superconducting phase corresponds to the number of normal states which have disappeared within Δ below E_F.[14]

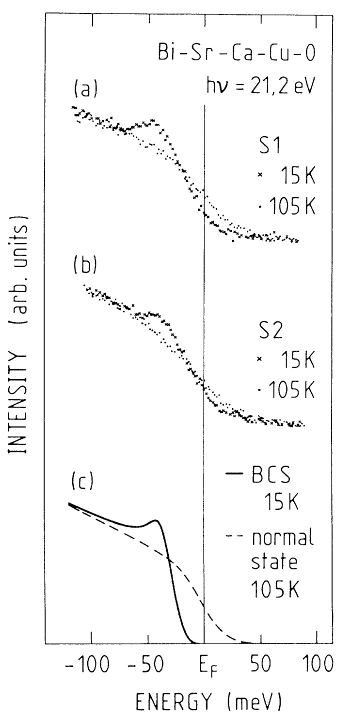

FIG. 3. (a) and (b) Comparison between the experimental spectra of Fig. 2 and (c) a model calculation of the density of states (see text).

In Fig. 3 we compare the measured spectra [Figs. 3(a) and 3(b)] of samples S1 and S2 [see Figs. 2(b)-2(e)] normalized at -120 meV, with a simple model calculation [Fig. 3(c)]. The normal-state curve for $T=105$ K has been simulated by the assumption of a linearly decreasing density of states convoluted with a Gaussian instrumental line of 20 meV (FWHM) and multiplied by the Fermi function. Comparison with the experiment confirms that this curve describes satisfactorily the photoemission spectra near E_F at 105 K. For $T \ll T_c$ the BCS density of the quasiparticle excitations in the superconducting state was calculated from the density of normal states observed below E_F.[14] It was convoluted with the instrumental-resolution function and multiplied by the Fermi function. Then, the value of the gap parameter Δ was varied until satisfactory agreement with the observed spectrum was obtained. The overall agreement between this simple model and the experiment, as displayed in Fig. 3, is striking. We obtain a gap parameter of $\Delta=30\pm5$ meV, corresponding to a reduced gap parameter $2\Delta/k_BT_c=8\pm1.4$. This value is much larger than the BCS prediction of 3.5 in the weak-coupling regime but lies within the range of values obtained by low-energy techniques which might not yield the same information. The interpretation of such spectra as revealing the formation of a gap is corroborated by the observation that the intensity increase corresponding to the peak is about equivalent to the intensity decrease in the Fermi-energy region, as shown in Figs. 3(a) and 3(b) by the comparison of the spectra recorded at 15 and 105 K. We believe that the spectral modifications reported in Ref. 10 do not have the same origin.[15]

However, the agreement between the model calculations and the spectra is by far not perfect. In the superconducting state, the spectra clearly show a finite intensity in the gap which cannot be attributed to the instrumental resolution, as demonstrated by the comparison with the steep Fermi edge of Cu at 15 K [Fig. 2(a)]. Since it is known that the crystals cleave between the two Bi-O planes,[16] we tentatively ascribe this intensity in the gap to states belonging mainly to the nonsuperconducting layers[17,18] between the surface and the first Cu-O plane. At all events, we have found an experimental confirmation that this intensity is originating from the first surface layers whereas the superconducting signal accounts for states located deeper below the surface. By changing the electron takeoff angle from the direction normal to the surface to 45°, the escape depth of the emitted electrons is decreased by 30%. The consequence is a clear weakening without energy shift of the peak at −30 meV whereas the low-energy flank of the spectrum is not modified. Qualitatively the same effect has been observed for the two samples.

In this Letter we have presented the first high-resolution photoemisison spectra of the low-lying quasiparticle excitations which reflect specifically the superconducting state of Bi-Sr-Ca-Cu-O. The comparison of these data with a simple model for the density of states above and below T_c provides a strong evidence for the opening of a superconducting gap with a reduced value $2\Delta/k_B T_c = 8 \pm 1.4$. We hope in the nearest future to be able to contribute to the elucidation of the superconducting mechanism in this compound by measuring the temperature dependence of the gap.

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