Anomalous Spectral Weight Transfer at the Superconducting Transition of $Bi_2Sr_2CaCu_2O_{8+\delta}$

D. S. Dessau, B. O. Wells, Z.-X. Shen, and W. E. Spicer
Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

A. J. Arko and R. S. List[(a)]
Los Alamos National Laboratories, Los Alamos, New Mexico 87545

D. B. Mitzi[(b)] and A. Kapitulnik
Department of Applied Physics, Stanford University, Stanford, California 94305
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Anomalous spectral weight transfer at the superconducting transition of single-crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ was observed by high-resolution angle-resolved photoemission spectroscopy. As the sample goes superconducting, not only is there spectral weight transfer from the gap region to the pileup peak as in BCS theory, but along the Γ-$\overline{M}$ direction there is also some spectral weight transfer from higher binding energies in the form of a dip. In addition, we note that at the superconducting transition there is a decrease (increase) in the occupied spectral weight for the spectra taken along Γ-$\overline{M}$ (Γ-X).

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In the BCS theory for traditional superconductors the electron Fermi sea is unstable to attractive interactions mediated by phonons. A superconducting gap is formed when the near-Fermi-edge electrons condense to form pairs at low temperatures. As illustrated in the inset of Fig. 1, the spectral intensity in the region from the Fermi energy to an energy Δ is lost at the transition to superconductivity. This spectral weight is transferred to a region just below the gap (higher binding energy) and thus there is a pileup of intensity in this region. In this Letter we report results from photoemission studies of high-quality single-crystalline samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (with different values of δ) which show an anomalous transfer of spectral weight at the superconducting transition which is not consistent with the conventional BCS picture. For this compound we found that not only is there a spectral weight transfer from the gap region into the pileup at the superconducting transition, but for spectra taken along the Γ-$\overline{M}$ **k**-space direction a dip appears at higher binding energies. In addition, we note that at the superconducting transition there is a decrease (increase) in the occupied spectral weight for the spectra taken along Γ-$\overline{M}$ (Γ-X). These effects are reproducible and strongly dependent upon the doping level of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples.

Very-high-quality single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ were grown by the directional solidification technique. The crystals studied in this report were annealed either in a 0.1% H_2 in Ar gas mixture at 450 °C to raise the T_c to 91 K as determined by low-field magnetic susceptibility measurements, or in 12 atm of O_2 at 540 °C to lower the T_c to 79 K. Details of the sample preparation process and characterization are available elsewhere.[1] Single crystals of the material of about 1.5 mm × 1.5 mm

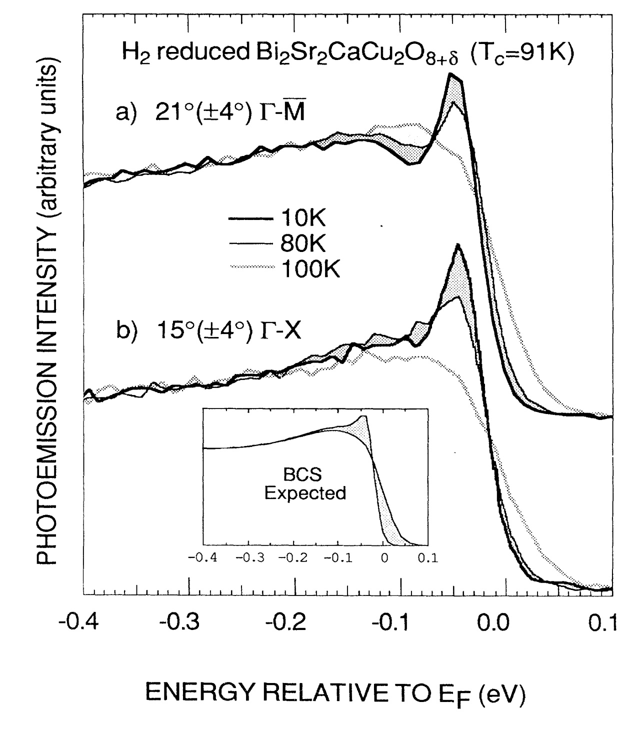

FIG. 1. Angle-resolved photoemission spectra taken at three different temperatures near the Fermi surface (a) along Γ-$\overline{M}$ and (b) along Γ-X. The spectra have been normalized to equal intensities for energies less than -0.2 eV. Inset: Illustration of the spectral weight transfer at the superconducting transition of the simple-coupling BCS theory, for a gap $\Delta = 27$ meV. The line shape of the normal-state spectra is analogous to that of the experiment, and is then multiplied by the BCS function to obtain the line shape of the superconducting state. An instrumental broadening of 40 meV has been included.

$\times 0.1$ mm were epoxyed to sample holders that were screwed into our cryostat. Top posts were epoxyed to the sample surface. The crystals were cleaved in a vacuum of 1×10^{-10} torr at approximately 10 K by knocking off the top post. Photoemission spectra were recorded by a Vacuum Science Workshop (VSW) hemispherical analyzer with an acceptance angle of $\pm4°$ and equipped for multichannel counting. The combination of multichannel counting, long counting times, and fairly large angular acceptance was used in order to increase the signal-to-noise ratio and allow us to take data with adequate statistics to observe the features reported here. Photons of energy 21.2 eV were obtained from a He discharge lamp. The total system energy resolution was approximately 40 meV as determined by the 10%–90% transition of a Au Fermi edge measured at 10 K. The Fermi energy was frequently monitored by measuring a Au film deposited on the cryostat beside the sample.

Earlier angle-resolved photoemission experiments on $Bi_2Sr_2CaCu_2O_{8+\delta}$ have clearly observed dispersive bands which cross the Fermi level at approximately the angles predicted by band theory.[2-5] It is near these angles, where there is spectral strength at the Fermi level, that the effects of the superconducting gap can be seen. Therefore, that is the general region where we have concentrated our study. Figure 1 shows temperature-dependent[6] near-Fermi-edge photoemission spectra of a H_2-reduced $Bi_2Sr_2CaCu_2O_{8+\delta}$ sample at $21°(\pm4°)$ along Γ-$\overline{M}$ (near the $\overline{M}$ point) and at $15°(\pm4°)$ along Γ-X. Slight corrections in the relative overall intensities of the spectra were made so that the intensities coincided at energies below -0.2 eV in each panel of Fig. 1.[7] As the sample temperature is lowered through its superconducting transition temperature (91 K) very dramatic spectral line-shape changes are observed. As expected by conventional pairing theories, spectral weight is transferred (for both **k**-space locations) from the gap region (approximately 0 to -20 meV), to a pileup peak at about -45 meV. However, at 21° along Γ-$\overline{M}$ spectral weight is also depleted from a region centered at approximately 90 meV below the Fermi level. We note that the diplike feature at -90 meV appears *only* below T_c and then increases in strength as the sample temperature is further lowered. It is not present at temperatures only slightly above T_c, and so we conclude that it must be directly related to the sample going superconducting. This diplike feature is very weak or not present in the spectra taken at 15° along Γ-X. We note that we have repeated these measurements on four H_2-reduced $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples, all of which gave very similar results. We have also studied $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples that had been annealed in 12 atm of oxygen which increases the hole concentration but decreases the T_c of the sample to 79 K.[1] While the -90-meV dip is still clearly present along Γ-$\overline{M}$ in these samples, it appears with much reduced strength.

A further very interesting aspect of our data is that the amount of spectral weight that we gain in the pileup peak does not appear to be equal to the weight that we lose from other regions (the gap plus dip). Along Γ-X we gain more weight in the pileup, while along Γ-$\overline{M}$ we gain less weight. Though there are complicating factors that could be involved, such occupied spectral weight changes would not to first order be expected in the conventional picture, and so may signal new and interesting physics. Interestingly, the departure in spectral weight conservation appears to be less pronounced for the 12-atm O_2 annealed samples that we have studied, which is likely consistent with the smaller dip observed along Γ-$\overline{M}$ and the lower T_c of the samples.

A number of groups have reported the observation of the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$ by photoemission,[2-4,8-10] and hints of such an anomalous spectral weight transfer such as we detail here did in fact exist in some of these earlier data. Olson *et al.* showed temperature-dependent data that are very similar to our data along Γ-X, including a larger area under the pileup peak than was depleted from the gap region.[2,9] Some of Olson *et al.*'s more recent data on $T_c=85$ K $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples also seem to show the same dip at -90 meV along Γ-$\overline{M}$, though their statistics were not nearly as good as ours and a temperature-dependent study was not done.[9] In addition, tunneling spectroscopy, which also reveals information about the spectral weight function, has shown similar temperature-dependent effects on $YBa_2Cu_3O_7$ thin films—with decreasing temperature, spectral weight is removed from the gap region and piles up at higher energies, along with a concurrent depletion of spectral weight from higher binding energies.[11] Important differences between our data and the tunneling data are that the energy scale of the features in their data is smaller than ours, and, since tunneling effectively averages over all **k**'s, they could not supply information about the **k** dependence of these effects.

A careful examination of our data shows that the edge in the superconducting state is pushed back farther from the Fermi level in the Γ-$\overline{M}$ data than in the Γ-X data. This is a strong indication of *a*-*b*-plane superconducting-gap anisotropy. To gain further insight into this, we have done some fitting of our data. For lack of anything better we have assumed a BCS line shape in the superconducting state and have approximately followed the method of Olson *et al.*[2] though we have tailored our fits for optimization at the near edge only, which gives slightly different looking fits from those of Ref. 2. With reservations on the significance of the numbers, we have obtained values for the gap of approximately 27 meV for the spectra along Γ-$\overline{M}$ and 15 meV for the spectra along Γ-X. Using the Eliashberg equations, Arnold, Mueller, and Swihart have independently done a full inversion of our data along both Γ-$\overline{M}$ and Γ-X and arrived at gap values and anisotropies that are qualitatively similar to those we have arrived at.[12] The differences in gap sizes in the a-b plane is a very important finding in its own right, and is yet another indication of the anisotropic nature of the superconducting excitations. Details of our fitting efforts, including the differences caused by anisotropy and oxygen doping, as well as a comparison to prior work,[9] will be discussed in a followup paper.

The fact that the photoemission line-shape changes are so dependent on **k**-space location is very important, though the origin of the observed anisotropies is not yet known. We have previously shown that at least some of the states along Γ-$\bar{M}$ have significant Bi-O character, while those along Γ-X do not, and therefore are presumably Cu-O derived.[10] However, our normal-state dispersion studies[5] have been unable to detect the Bi-O derived electron pocket centered at $\bar{M}$ which single-electron-band-theory calculations[13] predict.

Thus there are two very interesting aspects of our data that require attention, keeping in mind the observed a-b-plane anisotropy in the line shape and the gap size. The first is the general issue of spectral weight transfer and the second is the appearance of the -90-meV dip in the data along Γ-$\bar{M}$. While these two aspects of our data are very likely interconnected, we do not feel that they are necessarily so, and so we will discuss them independently.

First, let us address the -90-meV dip that appears in the spectra along the Γ-$\bar{M}$ high-symmetry direction. The simplest explanation for this effect is that there are two bands in close proximity to each other along Γ-$\bar{M}$, and by coincidence they superimpose to form one feature in the normal state. As the temperature is lowered, one or both of these bands sharpen up (due perhaps to reduced lifetime broadening due to decreased electron-electron scattering in the superconducting state) and the dip appears between them. However, we have also taken data (which we will publish in a later paper) with $\pm 1°$ angular resolution all along Γ-$\bar{M}$, and in the normal state we see clear band dispersion and strong intensity modulations as a function of emission angle, *though we always observe only one feature*. In the superconducting state we observe a pileup peak and a dip for all angles where there is normal-state intensity at the Fermi level, though the relative intensities of the pileup peak and the dip depend strongly on the exact nature of the normal-state curve. Thus the simple explanation of two bands in the normal state which by coincidence superimpose to appear as one appears to be unlikely, although we cannot definitively rule it out. We feel instead that the dip is most likely an intrinsic feature of the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$ and may even be one of the keys to our understanding of the mechanism of the high-temperature superconductivity. We feel that it therefore deserves concerted theoretical as well as experimental attention.

In fact, a fair amount of theoretical attention has already been given to the problem. Arnold, Mueller, and Swihart feel that the dip may be related to the high-energy (relative to the pileup peak) oscillations observed in the tunneling spectra of the strong-coupling superconductors such as Pb and Nb. In these materials, the phonon spectrum $\alpha^2F(\omega)$ can be obtained from an inversion of the data using the Eliashburg equations.[14,15] Arnold, Mueller, and Swihart have assumed that a similar inversion process on our photoemission data can give an effective $\alpha^2F(\omega)$ for the high-temperature superconductors, whether or not phonons are responsible for the superconductivity. They claim good fits to our data along both Γ-$\bar{M}$ and Γ-X, T_c's that closely match the measured values and gap values in qualitative agreement with those we determined using the simpler weak-coupling BCS model.[12]

Anderson has some very interesting ideas about the origin of the dip. He writes that due to the hopping matrix element connecting the two close Cu-O layers (or the Cu-O planes with the Bi-O planes) in Bi_2Sr_2-$CaCu_2O_{8+\delta}$, there is a doubling of the *calculated* energy bands at general points in the two-dimensional zone with a splitting of order 0.1 eV, though the splitting nearly vanishes along the Γ-X symmetry direction. The fact that this splitting has not been observed in angle-resolved photoemission is, he says, strong support for the two-dimensionally correlated non-Fermi-liquid theory of the normal state. In the superconducting state, the quasiparticle fermionlike nature of the electronic excitations is partially restored and the three-dimensional band structure reappears. He thus .scribes the two features of the data along Γ-M (separated by the -90-meV dip) to quasiparticle poles belonging to odd and even linear combinations of states at the same transverse **k**, with the anisotropy of the results natural due to the details of the three-dimensional band structure.[16]

Finally, the phenomenological "marginal-Fermi-liquid" theory of Littlewood and Varma shows two peaks (one at Δ and one at 3Δ) in the calculated spectral weight function of the superconducting state, and thus the -90-meV dip that we observe may be due to a valley between these two peaks. According to their theory, the dip is not observed along Γ-X due to the much more rapid dispersion rates of the bands along that direction.[17]

Let us next discuss the issue of conservation of spectral weight at the superconducting transition. Anderson feels that the fact that the pileup along the Γ-X direction is larger than the weight lost from the gap region implies that there must have been a transfer of weight from higher binding energies (and that our normalization procedure was therefore incorrect).[16,18] While these are very interesting and exciting ideas, we caution that many experimental issues need to be clarified first. Among these are the fact that the weight in the pileup is *less* than the weight lost from other regions for the spectra along Γ-$\bar{M}$ (again, using our specific normalization procedure), final state or matrix element effects, and the possibility that spectral weight has been transferred to the unoccupied states. This last point is especially important since the sum rule that one expects to hold for a **k**-resolved experiment such as angle-resolved photoemission extends over both the occupied and the unoccupied states, whereas photoemission only measures the occupied states. The details of our efforts to correlate these problems will be published in the future.

In summary, we have used high-energy resolution, angle-resolved photoemission spectroscopy to detect anomalous spectral weight transfer at the superconducting transition of single crystalline $Bi_2Sr_2CaCu_2O_{8+\delta}$ (with different values of δ). Not only is there a spectral weight transfer from the gap region into the pileup peak at the superconducting transition but for spectra taken along the Γ-$\bar{M}$ **k**-space direction a dip appears at higher binding energies. In addition, we note that at the superconducting transition there is a decrease (increase) in the occupied spectral weight for the spectra taken along Γ-$\bar{M}$ (Γ-X). These effects are reproducible and appear to be strongly dependent upon the doping level of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples. This information may be important to our understanding of the microscopic mechanism of superconductivity.

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[a]Present address: Texas Instruments Inc., Dallas, TX 75265.

[b]Present address: IBM Thomas J. Watson Research Laboratories, Yorktown Heights, NY 10598.

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[7]Slight drifts of signal strength over time and especially between temperature changes (due to thermal expansion or contraction of the cryostat) are unavoidable, and so an exact experimental determination of spectral intensity is not possible. Note that these drifts will not affect the line shape of any particular spectrum, since each spectrum is an average of a large number of individual scans.

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