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Theoretical and experimental analysis of the superconducting transition effects on the Fermi-edge photoemission spectra

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We analyze the line-shape differences between $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ Fermi-edge photoemission spectra taken at room temperature and at temperatures below T_c. A quasiparticle theoretical approach indicates that these changes can be interpreted, in first approximation, in terms of a displacement of the leading edge, reflecting the creation of a superconductivity gap of a few tens of millivolts.

Photoemission spectroscopy has been extensively used to explore the electronic structure of high-temperature superconductors.[1] In particular, there has been an extensive search for the effects of the superconducting transition on the near-Fermi-edge spectral line shape.[2] In the case of compounds in the $YBa_2Cu_3O_{7-x}$ family, the search was frustrated by the absence of a signal at the Fermi edge, except for samples cleaved at very low temperature.[2] Studies of this kind are extremely interesting, since the near-edge line shape is a potential source of information on the very mechanism of high-T_c superconductivity.[3] However, the measurement of these effects is made difficult by their small energy scale in ordinary superconductors, and only recently has it become feasible to perform this study on the oxide superconductors.

In this article we discuss the nature of the temperature effects that might be expected and present preliminary evidence for their existence. A complete description of the photoemission process for electrons in the superconducting state is, of course, a formidable challenge to theory. Here, we propose a first-approximation quasiparticle model, based on the assumption of weak coupling. The assumption may be questionable for high-T_c materials. Nevertheless, preliminary experimental tests on $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ appear consistent with our main theoretical prediction. The model predicts that the leading spectral edge moves to lower energy as the temperature is lowered, due to the creation of the superconductivity gap, 2Δ. The observation of the shift is complicated by the limited energy resolution. We do, however, find differences between the room-temperature and low-temperature spectra which can be explained by the predicted shift, whereas they are not explained by the mere temperature dependence of the Fermi-Dirac function.

Experiments of this kind could not be performed on the "early" high-T_c materials such as $YBa_2Cu_3O_{7-x}$ since their spectra did not exhibit significant intensity at the Fermi edge, unless cleaved at very low temperature.[1,2] Our observation[4] of a distinct Fermi edge in the spectra of $Bi_4Ca_3Sr_3Cu_4O_{16-x}$ made this compound an obvious candidate to search for Fermi-edge modifications. The spectral region affected by such changes is determined by the magnitude of Δ. Thus, its width is 1 order of magnitude smaller than the energy resolution of a typical photoemission experiment. Therefore, energy resolution is another critical problem in the search for near-edge line-shape changes with temperature. The resolution can be improved using specialized equipment, but the consequent decrease in signal level increases the risk of sample contamination problems, particularly at low temperature. Note, however, that *shifts* of specific spectral features, i.e., peaks or—as in the present case—leading edges, can be observed even if they are orders of magnitude smaller than the intrinsic or instrumental broadening. This, for example, is routinely done in modulation spectroscopy.[5] In the present study, the energy resolution was sufficient to detect temperature effects without risking severe contamination problems.

A proper theoretical treatment of the photoemission process requires different descriptions for the normal state and the superconducting state. Specifically, it is not possible to assume *a priori* that the photoemission spectra of a superconductor reflect the one-electron density of states. Furthermore, for the normal state, the near-edge line shape could be significantly different for a resonating-valence-bond system and for a normal metallic (i.e., Fermi liquid) system.[3] These possible differences are still being analyzed, both theoretically and experimentally, and will not be considered in detail here. In either case, it is predicted that the spectra extend up to the Fermi edge for the normal state.[3] In our study, we will compare the normal-state spectra and the superconducting-state spectra, assuming a simple metallic nature for the Fermi edge of the normal state.

We will now consider the photoemission process from the superconducting state ($T=0$ K), using a quasiparticle approach. The photoemission process is described by the perturbation Hamiltonian $H'=hc_v^{\dagger}c_s$, where h is proportional to the photon field strength, and $c_v^{\dagger}, c_s$ are the creation operator of an electron in vacuum and the destruction operator of an electron in the superconductor. In turn, c_s can be expressed in terms of the creation and destruction operators of quasiparticles. Neglecting the quasiparticle destruction term because of the low number

of thermally excited quasiparticles, $c_s \sim v_k \gamma^{\dagger}_{-k}$, where v_k is a coefficient and $\gamma^{\dagger}_{-k}$ is a quasiparticle creation operator.

The corresponding photoelectron spectral distribution, $I(E)$, derived from the Fermi "golden rule," is proportional to $\sum_k v_k^2 \delta(E+E_k)$, where E is the photoelectron energy (measured from the Fermi level), and E_k is the quasiparticle energy.[6] In turn, this expression is proportional to $\int \rho(\varepsilon_k) v_k^2(\varepsilon_k) d\varepsilon_k \delta(E+E_k)$. Here ε_k is the one-electron (Fermi liquid) energy relative to E_F, the Fermi level, and ρ is the normal-state density of states. The energy ε_k is related to the quasiparticle energy by $E_k = (\varepsilon_k^2 + \Delta^2)^{1/2}$, i.e., $\varepsilon_k = \pm (E_k^2 - \Delta^2)^{1/2}$.

We have, therefore,

$$\rho(\varepsilon_k) d\varepsilon_k = \rho[\pm (E_k^2-\Delta^2)^{1/2}] \, | \, d\varepsilon_k / dE_k \, | \, dE_k$$
$$= \rho[\pm (E_k^2-\Delta^2)^{1/2}] [E_k/(E_k^2-\Delta^2)^{1/2}] dE_k \, .$$

Thus, for $E < -\Delta$, we obtain

$$I(E) \propto \{v_k^2[-(E^2-\Delta^2)^{1/2}]\rho[-(E^2-\Delta^2)^{1/2}] + v_k^2[(E^2-\Delta^2)^{1/2}]\rho[(E^2-\Delta^2)^{1/2}]\} \, | \, E \, | / (E^2-\Delta^2)^{1/2} \, ,$$

and $I(E) = 0$ otherwise.

Assume, in first approximation, that the normal-state density of states is constant in the neighborhood of E_F. Then, since $v_k^2[-(E^2-\Delta^2)^{1/2}] + v_k^2[(E^2-\Delta^2)^{1/2}] = 1$,[6] for $E < -\Delta$ we have $I(E) \propto |E|/(E^2-\Delta^2)^{1/2}$—the BCS function. Thus, under the above assumptions and approximations, we predict that the photoemission edge line shape for the superconducting state corresponds to the BCS function. In particular, the line-shape changes when the temperature is lowered below T_c should reflect the creation of the superconductivity gap. Once again, this is a somewhat surprising result which cannot be trivially derived using a one-electron picture.

We performed preliminary tests of this last conclusion by taking near-edge photoemission spectra of $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ at room temperature, and then at a temperature well below T_c, and comparing the results. The sample growth procedures are described in detail in Ref. 7. The resulting sintered and single-crystal specimens were determined to be single phase, with sharp superconducting transitions at 85 K, which were measured resistively and magnetically. The sample cooling system was a closed-circuit helium refrigerator, connected to the sample holder with a copper braid. This system enabled us to perform the cleaning procedures both at room temperature and at low temperature. The photoemission spectra were taken with a double-pass cylindrical mirror electron energy analyzer, which accepted photoelectrons over a large solid angle. The photoelectrons were excited with photons emitted by the Aladdin storage ring at the Wisconsin Synchrotron Radiation Center, filtered with a Seya-Namioka monochromator. With a photon energy of 25 eV, the overall spectral resolution derived from the metallic Fermi edge corresponded to a Gaussian full width at half maximum of the order of 190 meV.

The experiments were performed on 13 different surfaces cleaned under ultrahigh vacuum, including cleaved single-crystal specimens and sintered pellets scraped with a diamond grinder. Figure 1 shows typical results for two different single-crystal surfaces. Note the decrease in signal on the right-hand side as the temperature decreases. Considering the resolution, this suggests a downward shift of the leading edge, as predicted by the model. The changes were observed both by increasing the temperature of samples cleaned while cold, and by cooling samples cleaned at room temperature. The two sets of data of Fig. 1 were obtained with the second procedure, whereas the curves of Fig. 2 were obtained by increasing the temperature of a cold-cleaved sample.

Before discussing these results, we must address two important issues, those of sample contamination and normalization of the spectra. The possibility of contamination was quite real at low temperature, and we empirically found that contamination-related spectra features became prominent after several hours. With the signal levels corresponding to our energy resolution, the noise-to-signal level required to observe the small temperature effects was achieved in less than 1 h per spectrum, avoiding serious contamination problems. We also found progressive contamination of the sample surface does *not* produce near-E_F changes like those shown in Figs. 1 and 2. On the contrary, severe contamination tends to suppress such

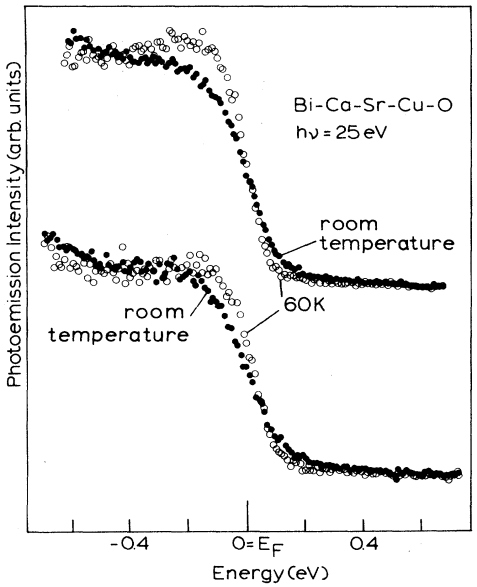

FIG. 1. Photoemission spectra taken at room temperature and at a temperature below the superconducting phase transition, 85 K, for two different $Bi_4Ca_3Sr_3Cu_4O_{16+x}$ single crystals, cleaved under ultrahigh vacuum. The spectra were taken with a photon energy of 25 eV, by cooling the samples after cleaving at room temperature. The normalization procedure is discussed in the text.

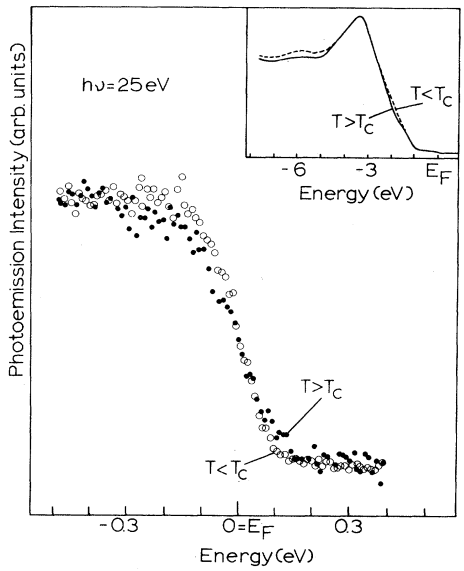

FIG. 2. Data similar to those of Fig. 1, obtained by increasing the temperature of a cold-cleaved sample. Inset: another set of data over a more extended spectral range, taken below the critical temperature and at approximately 150 K.

temperature-related effects.

The inset of Fig. 2 shows an example of valence-electron spectra taken before and after increasing the temperature of a cold-cleaned sample. Only small changes are observed—close to the limits in sample position reproducibility after temperature modifications—and severe contamination is ruled out. The changes after recooling the sample were even smaller. We found no correlation between these small changes and the near-E_F effects, which only tracked the temperature increases and decreases. However, even small changes in the tails of the main valence-electron features can significantly affect the weak signal in the region below E_F, thereby creating a possible normalization problem.

The spectra of Fig. 1 have been arbitrarily normalized to the region 0.4–0.5 eV below E_F, which corresponds to a relatively flat portion of the spectra, reflecting the plateau of the Fermi-Dirac function. We carefully analyzed other possible normalization criteria and their effects, e.g., normalizing to the main valence photoemission peak or to the same area. We found that the right-hand-side decrease in intensity with the temperature is present for all reasonable normalization criteria. Different normalizations, however, do significantly affect the apparent signal increase at lower energies. We decided, therefore, not to include this increase in our data interpretation. Note, however, that a signal increase at lower photon energies is expected from our theoretical line shape, after convolution with the instrumental response function.

The changes with temperature of the leading spectral edge were analyzed in three different ways. First, we compared them with the convolution of the instrumental response function with the Fermi-Dirac function. In this way, we found that the temperature dependence of the Fermi-Dirac function does not explain the observed changes.

Second, we tried to best fit the low-temperature line shape using the convolution of the BCS function with the instrumental response function. We found that a reasonable fit can be obtained by using values of Δ in the range 20–40 meV. In Fig. 3, for example, we show the BCS function for $\Delta = 30$ meV (dashed lines), together with the Fermi-Dirac line shape at room temperature (solid line), before and after convolution with the response function. Third, we used the iterative Bayesian deconvolution procedure to estimate the leading-edge positions at low temperature and at room temperature.[8] After extrapolating to the limit of no instrumental broadening, we estimate that the edge shift Δ is 15–45 meV. Therefore, two different kinds of data analysis agree in deriving from our data an edge shift of the order of a few tens of millivolts. Note that this shift tends to underestimate the actual width of the gap. In fact, the gap increases with the distance from the surface and it reaches the bulk value over a distance of the order of the coherence length. The coherence length perpendicular to the cleavage plane is very small in these materials ($\ll 10$ Å), and shorter than the photoelectron escape depth. Nevertheless, the narrowing of the gap in the surface region can affect the estimated edge shift.

Although our data analysis is based on a weak-coupling theory, we note that the observed changes do not suggest area conservation, i.e., that the signal increase at low en-

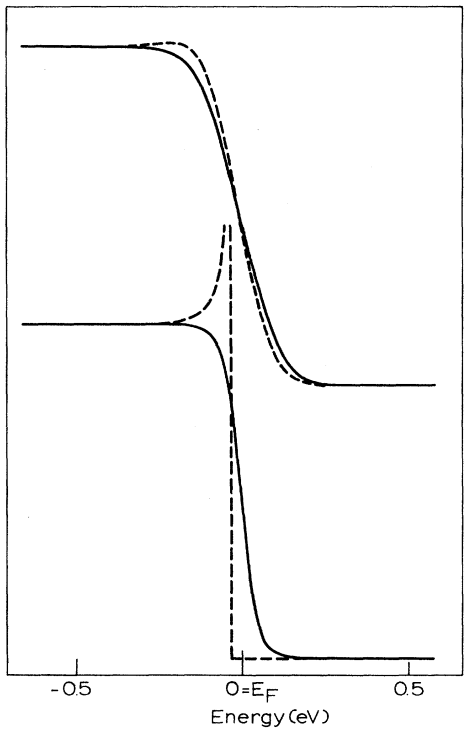

FIG. 3. Calculated curves using our data analysis. Bottom: Fermi-Dirac function at room temperature (solid line), and BCS function for $\Delta = 30$ meV (dashed line). Top: the corresponding curves, after convolution with a Gaussian function approximating the instrumental spectral response.

ergies outweighs the signal decrease at high energies. This is not unreasonable because for a high Δ/T_c ratio weak coupling is unlikely, whereas weak-coupling theories assume infinite lifetime for the quasiparticles, and therefore, a one-to-one correspondence between the electronic states in the normal and superconducting phases. In general, the nonconservation of the area is consistent with strong-coupling theories not based on a quasiparticle picture.[9]

The observation of temperature-induced changes in the near-edge line shape may open up exciting prospects for future research. Specifically, it may be possible to use photoemission for direct tests of different theories of high-temperature superconductivity. Before reliably performing such tests, some preliminary steps are necessary. For example, it is necessary to extend the theoretical description of photoemission from the superconducting state beyond the quasiparticle boundaries. It is necessary to improve the energy resolution, as much as allowed by possible contamination, to study the details of the spectral changes. Similarly, contamination permitting, it would be desirable to use angular resolution and study the k-space dependence of the temperature effects,[8,10] extending the elegant room-temperature work recently presented by Takahashi *et al.*[11] The specific temperature at which these phenomena occur must be pinpointed, and the experiments must be extended to other materials.

At this preliminary stage, however, our study has already established two important points. First, that temperature changes not explained by the Fermi-Dirac function exist in the near-edge spectra. Second, that their interpretation in terms of the gap creation appears theoretically justifiable as a first approximation. Future stages of this study pose formidable technical challenges, but they could provide significant contributions to the understanding of high-temperature superconductivity.

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