Temperature Dependence of the Energy Gap in $Bi_2Sr_2CaCu_2O_8$ Superconductors by High-Resolution Electron-Energy-Loss Spectroscopy

Yonghong Li, Jin Lin Huang, and Charles M. Lieber
Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138
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High-resolution electron-energy-loss spectroscopy has been used to determine the magnitude and temperature dependence of the energy gap for oxygen-annealed $Bi_2Sr_2CaCu_2O_8$ single crystals. Below T_c, low-energy excitations are detected in the energy-loss spectra. These spectra are proportional to the frequency-dependent resistivity, $\rho(\omega)$, and thus the energy gap can be determined directly from the onset of $\rho(\omega)$. We find that at low temperature $2\Delta = 6kT_c$ and that Δ develops sharply for $T < T_c$. The similarity of these results to the predictions of models that consider spin interactions suggests that higher T_c's may be obtainable in this material.

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The magnitude, temperature dependence, and symmetry of the energy gap $\Delta(T,k)$ for the high-temperature copper-oxide superconductors remain the focus of intense investigation since $\Delta(T,k)$ provides essential insight into the microscopic mechanism of superconductivity. The magnitude of 2Δ determined from $YBa_2Cu_3O_{7-\delta}$ (YBCO) [1-5] and $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) [6-14] single crystals have spanned a wide range: $2\Delta = (0-12)kT_c$. Several recent investigations seem to converge upon a value of $2\Delta = (6-8)kT_c$ [1,3,8,9] although considerable controversy still exists concerning the nature of Δ [2,14]. Nevertheless, most of the reported values of 2Δ significantly exceed the weak-coupling BCS limit of $3.5kT_c$. A large value of the reduced energy gap, however, does not alone strongly constrain the mechanism of superconductivity since it could arise from a number of factors.

The temperature dependence and symmetry of Δ can provide much more powerful constraints on the mechanism of superconductivity, although there has been considerable experimental uncertainty in the details of $\Delta(T,k)$. Infrared [1] and high-resolution electron-energy-loss (HREELS) [3] studies of YBCO have suggested that Δ is only weakly dependent on T, and, surprisingly, that the gap excitation does not disappear above T_c. Photemission studies indicate that Δ may be weakly dependent on temperature for BSCCO samples [7,8], although analyses of the $\Delta(T)$ data have not been reported. Tunneling measurements suggest that $\Delta(T)$ in BSCCO is either BCS-like [12] or weakly dependent on temperature [11]. To clarify how the superconducting gap develops below T_c, we have carried out detailed temperature-dependent HREELS studies of BSCCO single crystals. We find in high-quality annealed crystals that the magnitude of 2Δ is $6kT_c$. More importantly, these data show that the energy gap opens sharply at T_c and exhibits little change in magnitude for $T/T_c < 0.9$. These results are compared to the predictions of conventional models and theories that consider spin interactions. The similarity of $\Delta(T)$ to this latter work suggests that higher T_c's may be obtainable in these materials.

BSCCO single crystals were grown from CuO-rich melts as described previously [15]. The crystals were annealed for several days at 545 °C in 12 atm of O_2. This annealing procedure yields samples that are significantly more homogeneous than the as-grown crystals. The transition temperatures and transition widths (90%-10%) were determined magnetically on all of the single-crystal samples before the HREELS experiments; the values were typically 88-89 and 4-6 K, respectively. The HREELS experiments were carried out using a spectrometer that has been described in detail elsewhere [3]. Briefly, the instrument has a fixed 90° scattering geometry, and was operated such that the inelastically scattered electrons within a 1°-1.5° lobe of the elastically scattered beam were analyzed. For this regime of small momentum transfer ($q = k' - k = 0.001-0.01$ Å^{-1}), dipole scattering theory [16,17] can be used to quantitatively analyze the results as discussed below. The BSCCO samples were mounted on a cryoprobe and cleaved within the spectrometer (6×10^{-11} torr) at 31 K. Similar temperature-dependent results were obtained on several independent oxygen-annealed samples. The spectrometer was calibrated and routinely tested using a cleaved TaS_2 sample that was mounted on the cryoprobe with the BSCCO samples.

A series of temperature-dependent electron-energy-loss spectra for a sample of BSCCO cleaved at 31 K are shown in Fig. 1; for reference a spectrum obtained on a TaS_2 crystal is also displayed. Immediately evident upon examination of the low-temperature BSCCO data is the broad energy-loss peak centered at 60 meV. The intensity of this loss feature is ≈ 4000 times less than the quasielastic peak at 0 meV. Similar low-energy excitations are not observed in the energy-loss spectrum for nonsuperconducting TaS_2. In addition, we find that as the BSCCO sample temperature is increased (from 31 K) the intensity of the loss feature at 60 meV decreases, and that this feature disappears when the temperature is raised above T_c. The 60-meV loss feature does, however, reappear when the sample is again cooled below T_c. On the basis of these temperature-dependent data we assign the

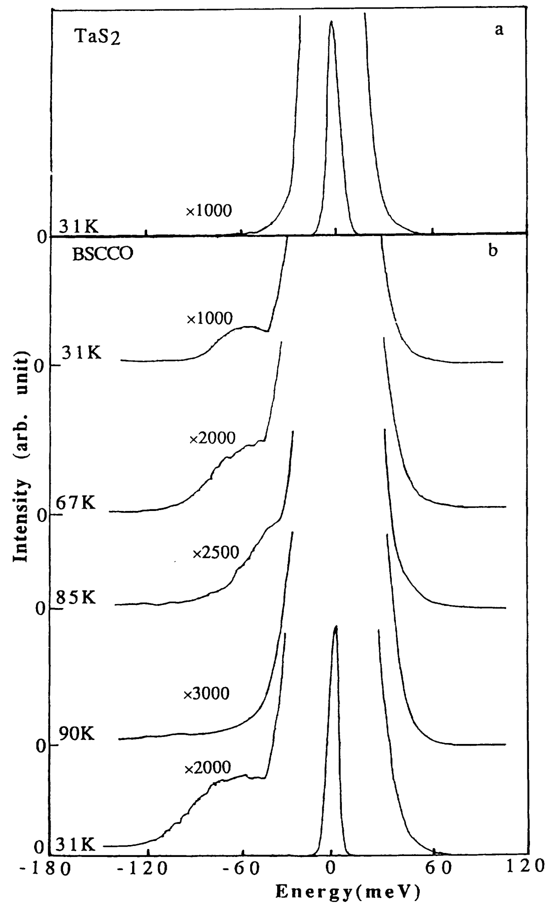

FIG. 1. (a) Energy-loss spectrum for TaS_2 obtained at 31 K. The resolution, which is defined as the full width at half maximum of the quasielastic peak, is 7.5 meV. At high sensitivity (×1000) no energy-loss features are observed on the tail of this peak. (b) Temperature-dependent energy-loss spectra of BSCCO recorded on a sample cleaved at 31 K. The resolution is 6.5 meV. The spectra recorded below T_c exhibit an energy-loss feature at −60 meV. The spectra were recorded sequentially from top to bottom.

new loss feature to pair-breaking excitations of energy 2Δ.

Previously, HREELS has been used with mixed results in efforts to determine 2Δ. For example, several studies have reported temperature-independent features consistent with optical phonons [10]. Demuth and coworkers have observed temperature-dependent energy-loss features on YBCO and BSCCO samples, as well as temperature-independent features [3]. We believe that the differences between our present results and previous studies can be explained by the high-quality samples used in this investigation. In support of this idea we note that the relatively high-resistivity surfaces of "as-grown" BSCCO samples (which poorly screen the electric field) exhibit the same weakly temperature-dependent optical phonons detected in earlier studies [18]. In contrast, our annealed BSCCO samples have low-resistivity surfaces that yield reproducible and reversible high signal-to-noise spectra from which we can readily determine 2Δ. These observations further reinforce the idea that detailed measurements should be carried out only on high-quality samples. Below we discuss the analysis of our data obtained on these annealed BSCCO crystals.

The energy-loss spectra can be analyzed by dipole scattering theory [16,17]. Using this formalism the electron scattering probability is $P(k,k')=A(k,k')(n_\omega+1)\times \mathrm{Im}g(\omega,q_\parallel)$, where $A(k,k')$ is a kinematic term independent of the sample, n_ω is the Bose-Einstein factor, and Img is the loss function. In general, the loss function is related to the dielectric properties of the material: $\mathrm{Im}g=\mathrm{Im}[-1/\{1+\varepsilon(\omega,q_\parallel)\}]$. A specific model for $\varepsilon(\omega,q_\parallel)$ is required to quantitatively calculate the loss function [3,16]; however, for a high conductivity surface Img will be proportional to $\omega\rho(\omega)$, where $\rho(\omega)$ is the frequency-dependent resistivity, independent of the details of this model [19]. Hence, the magnitude of 2Δ can be assigned to the onset of $\rho_s(\omega)$. Since this onset will be essentially independent of the detailed model chosen to represent $\varepsilon(\omega,q_\parallel)$, our experimental determination of 2Δ should be considered robust. In addition, we note that our analysis is more direct than either IR-reflectance spectroscopy (which requires Kramers-Kronig transformation of the data) or photoemission spectroscopy (which requires fitting to a model for the temperature-dependent

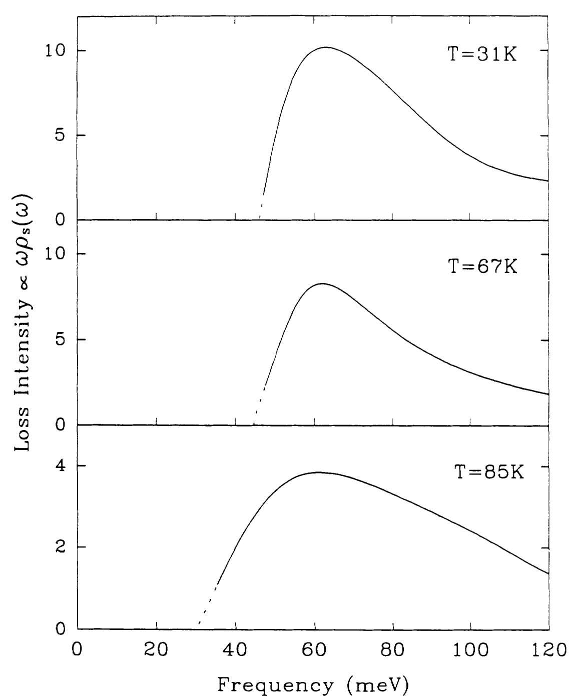

FIG. 2. Plots of the frequency-dependent resistivity obtained from the analysis of the data in Fig. 1. The solid lines correspond to the best fit of the energy-loss–energy-gain intensity. The dashed line is an extrapolation to the onset of $\rho_s(\omega)$.

density of states). In Fig. 2 we plot the difference of the energy-loss and energy-gain sides of the spectrum to remove background and statistical contributions to the spectra; these curves are proportional to $\omega\rho_s(\omega)$. The data exhibit a clear onset for the pair-breaking excitations [20]. The low-temperature limit (31 K) of the onset, 46.0 meV, yields $2\Delta = 6.0kT_c$. The magnitude of $2\Delta/kT_c$ is similar to values inferred from several photoemission, infrared, and tunneling measurements and supports our conclusion that the excitations detected in the HREELS spectra are pair-breaking excitations. The essential conclusions from this analysis are (1) that the experimental data are proportional to $\rho_s(\omega)$ and (2) that 2Δ can be equated with the onset of $\rho_s(\omega)$.

A new and key result of this study is the temperature-dependent behavior of 2Δ. From Figs. 1 and 2 it is apparent that 2Δ is only weakly dependent on temperature below T_c, although the gap closes rapidly at T_c. These results are quantitatively summarized in Fig. 3 [21]. A weak dependence of Δ below T_c has been reported for YBCO [1,3]. However, in contrast to this work we find that the pair-breaking excitations disappear at T_c and do

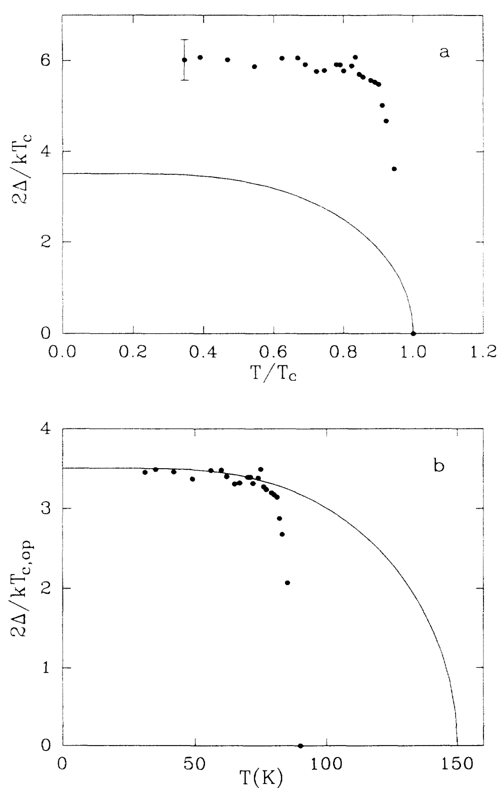

FIG. 3. (a) Temperature dependence of the reduced gap. The experimental data correspond to the solid circles. The solid curve is the behavior of $\Delta(T)$ predicted by BCS theory. (b) Plot of the experimental data (solid circles) scaled by $T_{c,\mathrm{op}}$ to yield a weak-coupling limit for the reduced energy gap. The solid curve corresponds to BCS prediction for $T_{c,\mathrm{op}} = 150$ K.

not persist above T_c. It is unlikely that this important diffrence could be attributed to an intrinsic difference between $\Delta(T)$ in YBCO versus BSCCO. In the previous HREELS experiment on YBCO it is possible that surface degradation in vacuum gave rise to an excitation close in energy to 2Δ that persisted above T_c. The difference between our HREELS and infrared measurements on YBCO will, however, require additional work to resolve. Regardless of these differences we note that our determination of 2Δ is straightforward from the raw data [20] and that the temperature dependence is reversible and reproducible in the annealed BSCCO samples. We thus believe that these data provide a strong constraint for theoretical models. Several possibilities are discussed below.

First, it is readily apparent that weak-coupling BCS theory [22] is inconsistent with the magnitude of Δ and the sharp opening of $\Delta(T)$ for $T \leq T_c$ [Fig. 3(a)]. A recent strong-coupling model proposed by Arnold, Mueller, and Swihart provides an excellent fit to $\Delta(T)$ for $T < T_c$ [23]. This model predicts, however, that Δ will persist above T_c and thus is in disagreement with our experiments [24]. In contrast to the inconsistent fits of our data obtained using conventional theory, there appears to be better agreement with recent models that consider spin interactions [25,26]. For example, the theory of Pines and co-workers, which is derived from an antiferromagnetically correlated Fermi liquid, predicts both large values of $2\Delta/kT_c$ and a sharp development of Δ below T_c [25]. These results agree qualitatively with our experimental data. Bandte, Hertel, and Appel have shown that dynamic pair breaking (e.g., single magnon scattering) can also yield a large value of $2\Delta/kT_c$ and a sharp development of Δ for $T < T_c$ [26]. An important consequence of these theories is that increased magnetic correlations depress T_c via pair-breaking scattering. Indeed, it is well known that pair-breaking or inelastic scattering processes will suppress T_c and $\Delta(0)$ [27]. Since T_c is reduced more rapidly than $\Delta(0)$, $2\Delta(0) > 3.5kT_c$. The sharp onset of $\Delta(T)$ at T_c found in our experiments strongly indicates that such inelastic processes are important in BSCCO. Hence, it is interesting to speculate whether it is possible to obtain a higher or optimal transition temperature, $T_{c,\mathrm{op}}$, in the absence of pair-breaking scattering. If we assume that the coupling interaction is weak, then $T_{c,\mathrm{op}}$ can be estimated from the weak-coupling limit for the reduced energy gap $2\Delta/kT_{c,\mathrm{op}} = 3.53$. Using the value of 2Δ determined in this study, we estimate that $T_{c,\mathrm{op}} = 150$ K for the BSCCO system [28]. It will be interesting in the future to consider whether the spin excitation spectrum and inelastic scattering processes can be manipulated to reduce pair breaking and enhance T_c.

In conclusion, we have used HREELS to determine the magnitude and temperature dependence of the energy gap. The energy-loss spectra can be interpreted in a straightforward manner as frequency-dependent resistivi-

ties, $\rho(\omega)$, and thus 2Δ is determined from the onset of $\rho_s(\omega)$. We have shown that at low temperature $2\Delta = 6kT_c$ and that Δ develops sharply for $T < T_c$. While these results are inconsistent with conventional theories, they strongly resemble the predictions of models that consider charge-spin interactions. The similarity of $\Delta(T)$ to this latter work suggests that higher T_c's may be obtainable in these materials.

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[18] It is interesting that transmission IR measurements on BSCCO exhibit a weak feature at $12kT_c$ (=85 meV) which persists above T_c [2]. The weakly temperature-dependent excitations that we detect in our high-sensitivity HREELS measurements of as-grown BSCCO samples are similar in energy (85–90 meV); however, we do not attribute these excitations to a gap since they persist to room temperature.

[19] In general, we can write $\varepsilon(\omega,q_\parallel) = 4\pi i\sigma(\omega)/\omega + \delta\varepsilon(\omega,q_\parallel)$, where $\varepsilon(\omega,q_\parallel)$ and $\sigma(\omega,q_\parallel)$ are complex numbers, and $\delta\varepsilon(\omega,q_\parallel)$ corresponds to the dielectric contributions from surface phonons and other excitations [16]. In the limit of high surface conductivity, which corresponds to our annealed BSCCO samples, the dielectric response reduces to $\varepsilon(\omega,q_\parallel) \approx 4\pi i\sigma(\omega)/\omega$. Thus $\mathrm{Im}[1/\{1+\varepsilon(\omega,q_\parallel)\}] = \mathrm{Im}[\omega/4\pi i\sigma(\omega)] \equiv (\omega/4\pi)\mathrm{Re}\rho(\omega)$; that is, we directly measure the real part of the complex resistivity in this paper.

[20] Sensitivity analysis shows that the errors in the onset energies are $< 10\%$.

[21] We also note that if 2Δ is assigned to the peak in the $\rho_s(\omega)$ data (Fig. 2), the same temperature dependence is observed although scaled to a larger value of the reduced energy gap, $2\Delta = 7.8kT_c$.

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[28] We can further test the validity of this idea by measuring $\Delta(0)$ in BSCCO samples with different T_c's. For example, increases in $2\Delta/kT_c$ as T_c is reduced would be consistent with our proposal.