Dependence of the Energy Gap on T_c: Absence of Scaling in the Copper Oxide Superconductors

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(Received 5 March 1993)

High-resolution electron energy loss spectroscopy has been used to investigate the energy gap (2Δ) in a series of oxygen-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals with critical temperatures ranging from 71 to 94 K. Temperature dependent energy loss spectra demonstrate that 2Δ develops sharply for $T < T_c$ in all of the samples, and that the magnitude of 2Δ exceeds significantly $3.5kT_c$. Furthermore, 2Δ decreases only slightly as T_c is reduced from 94 to 71 K, and thus, *$2\Delta/kT_c$ increases systematically as T_c decreases.* These results indicate that T_c may be reduced significantly by strong inelastic scattering in the current copper oxides.

PACS numbers: 74.72.Hs, 74.20.Mn, 74.25.Nf, 74.62.Dh

The mechanism of superconductivity in the copper oxide materials remains an open and controversial question [1-5]. One key property of the superconducting state that can in principle shed considerable light on the pairing interaction and mechanism is the energy gap, 2Δ. Considerable effort has been placed on determining the magnitude of 2Δ. Recent investigations of single crystal samples seem to converge on a value of $2\Delta \approx (5-7)kT_c$ [6-10], although the exact nature of this gap has not been resolved [10,11]. Nevertheless, it is clear that the energy scale for pair binding (2Δ) exceeds significantly the weak coupling of $3.5kT_c$, although a large value of 2Δ does not by itself strongly constrain the mechanism of superconductivity. The dependence of 2Δ on temperature and sample T_c can provide much deeper insight into the pairing interaction and mechanism of superconductivity. Recent measurements of $\Delta(T)$ in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) single crystals by high-resolution electron energy loss spectroscopy (HREELS) have shown (1) that the gap opens sharply below T_c, (2) that Δ remains relatively constant ($2\Delta \cong 6kT_c$) for $T < 0.8T_c$, and (3) that the gap does not persist above the bulk T_c [6]. On the basis of these $\Delta(T)$ results we have suggested that large values of $2\Delta/kT_c$ for the copper oxide materials may arise from pair-breaking scattering and not simply strong coupling [6]. Because pair breaking suppresses T_c but does not affect significantly $\Delta(0)$, measured values of $2\Delta/kT_c$ may exceed 3.5 even when the coupling is intrinsically weak. Hence, it is important to clarify the hole that inelastic scattering processes may play in determining superconductivity in the copper oxides.

One incisive test for the existence of pair breaking would be to determine how the magnitude of 2Δ scales with sample T_c. In general, it is expected that the ratio $2\Delta/kT_c$ will remain constant within a given class of materials, although in the presence of pair breaking $2\Delta/kT_c$ should increase as T_c decreases. In this Letter we establish clearly the relationship between 2Δ and sample T_c in a series of BSCCO high-T_c superconductor single crystals. High-quality single crystals with T_c's varying from 71 to 94 K have been prepared by oxygen annealing, and $\Delta(T)$ has been determined using HREELS. The magnitude of 2Δ at low temperature exhibits only a slight decrease as sample T_c is reduced from 94 to 71 K. *Importantly, these results demonstrate that $2\Delta/kT_c$ increases significantly as T_c decreases,* and thus indicate that strong inelastic scattering reduces T_c in the copper oxide superconductors.

Single crystals of the BSCCO superconductor were grown from Bi_2O_3 rich melts in high-purity MgO crucibles [12]. Thin single crystals were annealed in oxygen pressures of 0.2 to 50 bars at 540 °C for ca. 5 days to achieve variations of T_c from 94 to 71 K, respectively. X-ray diffraction, magnetization, and resistivity measurements were used to characterize the sample T_c and superconducting fraction, and to demonstrate that impurity phases did not form during the annealing process. Lower T_c's (i.e., < 71 K) can be achieved by higher pressure and/or higher temperature annealing; however, such conditions form impurity phases within the crystals. Representative magnetization and resistivity data for two distinct crystals are shown in Fig. 1. The narrow (~ 2 K) transition widths determined from magnetization measurements for these samples (among the sharpest reported for BSCCO) are indicative of high material homogeneity. In addition, the small extrapolated residual resistivities for these samples (1-2 $\mu\Omega$ cm) show that there is little impurity scattering. Hence, our oxygen-doped BSCCO samples represent an ideal series of materials in which to investigate the question of energy gap scaling.

The HREELS measurements of 2Δ were carried out using a spectrometer described previously [6,8]. The signal to noise ratio has been improved by > 10× using new pulse counting electronics since our initial study [6]. The instrument has a fixed 90° scattering geometry, and only electrons inelastically scattered within ≈ 1° of the specular beam are analyzed. This small angle or small momentum transfer ($q_\parallel = k'_\parallel - k_\parallel = 0.001$-$0.01$ Å^{-1}) scattering regime has been quantitatively treated using dipole scattering theory [8,13]. Briefly, the scattering probability at $T = 0$ K is $P(k,k') = A(k,k')\mathrm{Img}(\omega,q_\parallel)$, where $A(k,k')$ is a kinematic term that depends on instrument geometry and $\mathrm{Img}(\omega,q_\parallel)$ is the loss function. In general,

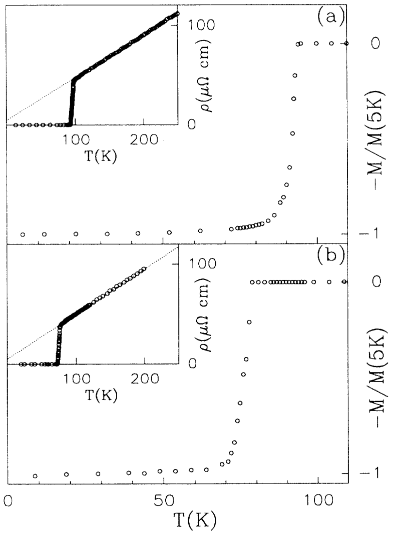

FIG. 1. Magnetization and resistivity measurements recorded on (a) $T_c=94$ K and (b) 77 K BSCCO samples. The susceptibility measurements were recorded in a field of 10 Oe. The insets show resistivity data for the same samples.

$\mathrm{Im}\,g(\omega,q_\parallel)$ can be equated with the frequency dependent dielectric response: $\mathrm{Im}(-1/[1+\varepsilon(\omega,q_\parallel)])$, where $\varepsilon(\omega,q_\parallel)=\varepsilon_\infty+4\pi i\sigma(\omega)/\omega+\omega_p^2/(\omega_{\mathrm{TO}}^2-\omega^2-i\Gamma\omega)$ [6,13,14]. In the limit of high conductivity, which is appropriate for metallic samples, $\varepsilon(\omega,q_\parallel)\approx 4\pi i\sigma(\omega)/\omega$ and $P(k,k')\propto\rho(\omega)$. Because the scattering probability is directly proportional to the frequency dependent resistivity, $\rho(\omega)$, it is straightforward to assign 2Δ as the onset of $\rho(\omega)$ [6].

Typical temperature dependent HREEL spectra recorded on $T_c=94$ K and $T_c=77$ K samples are shown in Fig. 2. Energy loss spectra recorded below the bulk sample T_c's show broad excitations centered around 60 meV at low temperature. The excitations disappear above the bulk T_c's, but reversibly reappear when the samples are cooled below T_c. Similar results have been obtained on all of the high-quality annealed samples with T_c's ranging from 71 to 94 K [15]. The disappearance of the energy loss features above the bulk sample T_c demonstrate that they are due to excitations in the superconducting state [6].

We can readily determine the energy gap from this data since 2Δ corresponds to the onset of $\rho(\omega)$: For $\omega>2\Delta$ a sharp increase in $\rho(\omega)$ due to pair-breaking excitations is expected. The frequency dependence of $\rho(\omega)$ was obtained by deconvoluting the elastic scattering peak $(\omega=0)$ from the energy loss spectra [6,16]. The curves shown in Fig. 3 correspond to a deconvolution of the spectra shown in Fig. 2; similar results were obtained for the different T_c samples. Several important conclusions can be drawn from the $\rho(\omega)$ data. The magnitude of 2Δ at low temperature, determined from the onset in $\rho(\omega)$, is unambiguous in the high-T_c samples and in ones in which T_c has been suppressed by over 20 K. The uncertainty in the onset of $\rho(\omega)$, ±2.5 meV, is also small [16]. A limitation in the HREEL experiment is that we do not have a quantitative model to fit the full frequency dependence of the loss spectra. However, the physics essential to this study is obtained directly from the onset of $\rho(\omega)$, and thus we believe that the results are robust.

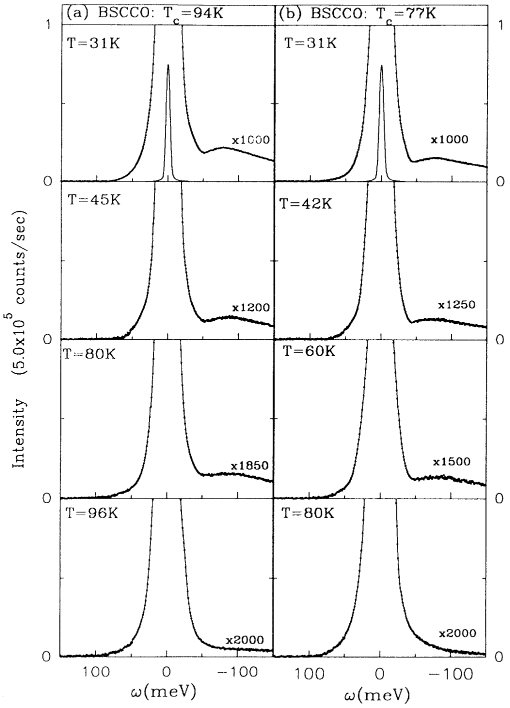

FIG. 2. HREEL spectra recorded on (a) $T_c=94$ K and (b) 77 K BSCCO crystals. The crystals were cleaved at 31 K immediately prior to the experiments, and spectra were recorded as the temperature was increased. The instrument resolution is ≈6.5 meV. The black dots correspond to the raw data and the solid lines to best fit curves through these data.

A new and central result obtained in this study is that 2Δ does not scale with T_c. The absence of scaling can be readily seen in the comparison of the temperature dependent gap data determined for the $T_c=94$ and 77 K samples [Fig. 4(a)]. At low temperature the reduced gap is larger for the $T_c=77$ K than the $T_c=94$ K sample: $2\Delta/kT_c=7.2$ vs 6.3, respectively. Similar results were obtained on samples with different T_c's and are summarized in Fig. 4(b). Importantly, we find that the uncertainty in 2Δ determined from the HREELS data is smaller than the change in 2Δ that would be expected if $2\Delta/kT_c$ were constant [16]. Because 2Δ decreases only slightly as the sample T_c decreases from 94 to 71 K, we find that $2\Delta/kT_c$ increases significantly with decreasing T_c.

The dependence of 2Δ on sample T_c has been investigated in previous studies [17,18]. Rotter *et al.*, used infrared reflectance (IR) spectroscopy to probe 2Δ in oxygen-depleted $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (YBCO) crystals [17].

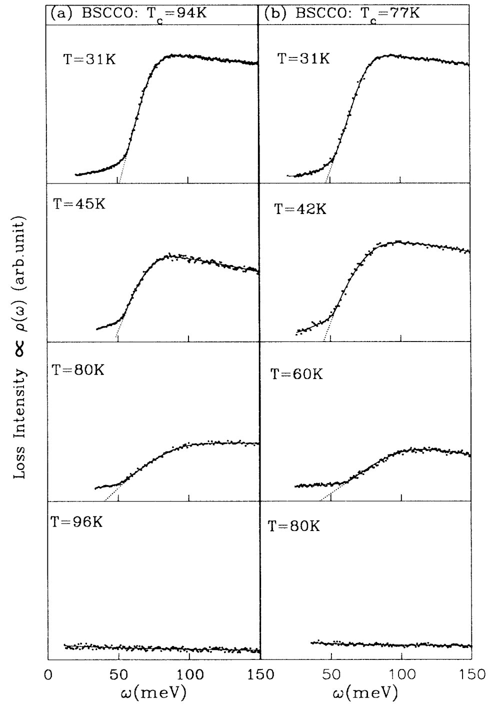

FIG. 3. Plots of the frequency dependent resistivity corresponding to (a) $T_c = 94$ K and (b) 77 K samples. The $\rho(\omega)$ vs ω curves were obtained by deconvoluting the elastic peak from the spectra.

They reported that the superconducting pair excitation threshold (2Δ) was nearly independent of T_c. These IR data appear similar to our results, although there has been considerable controversy over the interpretation of the IR results [7,19]. More recently, photoemission spectroscopy (PES) has been used to determine the energy gap in two distinct BSCCO samples [18]. In contrast to our studies, this work reported that the energy gap scaled with T_c. We believe that these differences are due to material and instrumental limitations in this previous work. The homogeneity of the two different T_c samples used in the PES study is unknown. We have shown that sample inhomogeneity may adversely affect the analysis of 2Δ [6,15]. In addition, the resolution of the PES experiments, 50 meV ($\approx 10\times$ larger than in our experiments), leads to greater uncertainty in the value of 2Δ. Our data show that $2\Delta/kT_c$ changes systematically in high-quality samples spanning a wide range of T_c's, and hence we believe that these HREELS results reflect the intrinsic behavior of the BSCCO system.

A key finding of our study is that $2\Delta/kT_c$ increases as T_c decreases. This result, the large magnitude of $2\Delta/kT_c$, and our observations that 2Δ opens rapidly at T_c are powerful constraints for models of superconductivity. The observed magnitude and behavior of $\Delta(T)$ and $2\Delta/kT_c$ are indicative of pair breaking. For conventional pair-breaking scattering by magnetic impurities [20], scattering rapidly suppresses T_c but not $\Delta(0)$. Hence, as the pair-breaking interaction is turned on and increased, $2\Delta(0)/kT_c$ increasingly exceeds the weak-coupling limit of 3.5. A fit of our data by this conventional model illustrates that significantly higher T_c's would be expected in the absence of scattering (Fig. 5). This comparison is made only to illustrate the phenomenological agreement with the behavior expected for standard pair-breaking theory. This conventional pair-breaking model is not,

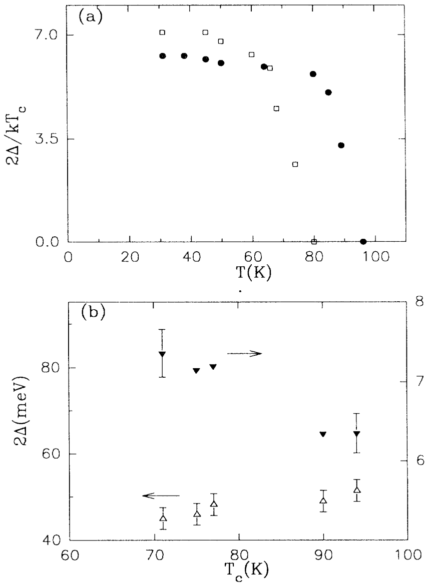

FIG. 4. (a) Plots of the $2\Delta/kT_c$ vs T data obtained for the $T_c = 94$ K (●) and $T_c = 77$ K (□) samples. (b) The values of $2\Delta/kT_c$ (△) and $2\Delta/kT_c$ (▼) obtained at $T = 31$ K for BSCCO single crystal samples with T_c's ranging from 71 to 94 K. Error bars reflect the uncertainty in 2Δ.

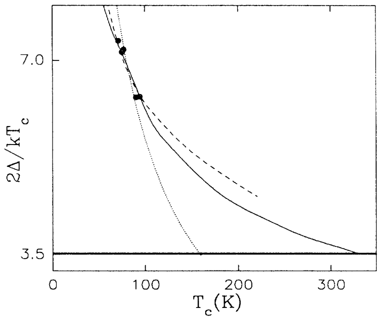

FIG. 5. Comparison of the experimental data with theoretical models. The heavy horizontal line ($2\Delta/kT_c = 3.5$) corresponds to BCS theory. The solid line corresponds to a fit using pair-breaking theory [20] assuming that $2\Delta = 3.5kT_c$ in the absence of pair breaking. The dashed line corresponds to the response predicted in [3] for $YBa_2Cu_3O_{7-\delta}$ (scaled to our data), and the dotted line corresponds to an extrapolation where 2Δ is constant.

however, applicable to these oxygen-doped BSCCO samples since the residual resistance is close to zero in these oxygen-doped samples regardless of T_c (Fig. 1). Hence, we believe that the oxygen dopants affect the inelastic scattering and pairing in a more complicated way.

One way to consistently explain these results is to use a model in which the excitations that result in strong inelastic scattering for $T > T_c$ (i.e., that suppress T_c) are the same excitations responsible for the pairing interaction. A theory developed for the copper oxide materials that explicitly treats such interactions is the antiferromagnetic Fermi liquid model of Pines and co-workers [2,3]. In this model spin fluctuations, which remain after doping the antiferromagnetic Cu (II) insulating state, strongly scatter quasiparticles in the normal state and thus suppress T_c. However, exchange of spin fluctuations also leads to an effective quasiparticle interaction and a superconducting state with $d_{x^2-y^2}$ symmetry. Calculations for YBCO predict that as T_c is reduced $2\Delta/kT_c$ should increase [2], as we observe for the BSCCO samples. It is interesting, although highly speculative, that an extrapolation of our results (using this model) to the limit of no pair-breaking suggests that T_c's near room temperature may be obtainable (Fig. 5). Clearly, further work is needed to quantitatively compare experiment and theory. For example, it will be important to determine the Cu and O spin susceptibilities for BSCCO samples having different T_c's; at present good data are only available for the YBCO and $La_{2-x}Sr_xCuO_4$ systems. An unambiguous determination of the symmetry of the superconducting state is also needed, although photoemission studies indicate that the pairing may have *d*-wave symmetry [21].

Regardless of these open issues, our HREELS studies provide essential new insight into the pairing interactions of the high-temperature superconductors. Measurements of 2Δ in a series of oxygen-doped BSCCO crystals demonstrate that 2Δ decreases only slightly and $2\Delta/kT_c$ increases systematically as T_c is reduced from 94 to 71 K. These data suggest strongly that pair-breaking interactions are intrinsic to the pairing mechanism of copper oxide superconductors. Viable theories for high-T_c superconductivity must account for these experimental results.

We would like to acknowledge M. Tinkham and J. E. Demuth for helpful discussions, and IBM for the loan of the HREEL spectrometer. C.M.L. acknowledges partial support of this work by the National Science Foundation through the Harvard NSF-MRL and DMR-89-19210.

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[14] This dielectric response $\varepsilon(\omega,q_\parallel)$ is taken for an isotropic material. Explicit account of the layered BSCCO structure does not change the essence of our interpretation: in the high-conductivity limit $P(k,k') \propto \rho(\omega)$ [8].

[15] Samples that exhibit broad ($\Delta T_c > 4$ K) transition widths often exhibit spatial variations in the energy loss spectra; e.g., we find high resistivity regions ($\approx 1000\ \mu\Omega$ cm) in which bulk phonon excitations are the dominant energy loss spectra [6]. Such high resistivity regions have undoubtedly contributed to uncertainty in previous measurements of 2Δ.

[16] Uncertainty in the deconvolution and assignment of 2Δ arises primarily from the fit of the quasielastic peak. Sensitivity analysis shows that the uncertainty in the onset to $\rho(\omega)$ is ± 2.5 meV. In addition, $\rho(\omega)$ curves have been determined by spectral subtraction [6]. The results from this procedure are virtually identical to those obtained by deconvolution, although the uncertainty is slightly larger: ± 3 meV.

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