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Tunneling and infrared measurements of the energy gap in the high-critical-temperature superconductor Y-Ba-Cu-O

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We have measured the superconducting energy gap Δ of high-critical-temperature ($T_c \sim 90$ K) $YBa_2Cu_3O_{9-y}$ samples using tunneling and infrared techniques. From our tunneling data, we place limits on the reduced superconducting energy gap of $3.7 < 2\Delta/k_BT_c < 5.6$. The tunneling gaps for a single-crystal sample are essentially the same if the tunneling tip is oriented either parallel or perpendicular to the CuO planes. The infrared measurements give a smaller apparent gap. We discuss the origins of the differences between the infrared and tunneling results.

In recent months the highest known superconducting critical temperature T_c has risen by a factor of 4, with hints of even higher transition temperatures. This dramatic development began when Bednorz and Müller reported possible superconductivity at 35 K in La-Ba-Cu-O samples.[1-3] Critical temperatures in the vicinity of 40 K were soon reported in La-Sr-Cu-O samples.[4-6] This was followed almost immediately by reports of critical temperatures near 90 K in Y-Ba-Cu-O samples.[7]

There have traditionally been two direct methods for measuring the energy gap in superconductors: tunneling and infrared techniques. Both have been used for the high-T_c superconductors $La_{2-x}Sr_xCuO_4$. The infrared reflectance and transmission experiments[8-10] showed energy gaps in the range $2\Delta/k_BT_c \sim 1.3-2.7$, well below the BCS prediction of $2\Delta/k_BT_c = 3.53$. Tunneling measurements,[11-14] sometimes on exactly the same samples, showed gaps in the range $2\Delta/k_BT_c \sim 3.5-6$, at least as large as the BCS prediction, and a factor of 2 larger than the infrared measurements.

We repeat these measurements for high-critical-temperature Y-Ba-Cu-O samples. These materials have superconducting critical temperatures of approximately 90 K, some 2.5 times higher than for the $La_{2-x}Sr_xCuO_4$ samples, and higher than had previously been believed possible with phonon-mediated electron-electron interactions.[15] We find that the tunneling gaps in Y-Ba-Cu-O samples are quite comparable in size to the BCS or a strong-coupling prediction. Furthermore, just as for $La_{2-x}Sr_xCuO_4$, the gaps observed using tunneling are larger than those estimated using infrared techniques. Although both the La-Sr-Cu-O (Ref. 16) and Y-Ba-Cu-O (Refs. 17-19) superconductors have anisotropic structures, with planar layers of Cu and O atoms which are believed to be responsible for the metalliclike conductivity, to date there have been no reports of tunneling into crystals as a function of crystal orientation. We show such data for Y-Ba-Cu-O here.

Polycrystalline Y-Ba-Cu-O samples were prepared by mixing BaO, Y_2O_3, and CuO in the appropriate proportions, pressing them into 12-mm-diam disks under 60000 psi of pressure, and sintering at 950 °C in air for 12 h followed by slow cooling.[20] Single crystals were picked from a sintered, partially melted pellet pressed from a slightly off-stoichiometric prereacted powder mixture of $YBa_2Cu_3O_{9-y}$.[21] Similar crystals picked from the same pellet showed twinning within the CuO planes but not in the direction of the principle $YBa_2Cu_3O_{9-y}$ structural anisotropy.[21] Although we performed both infrared and tunneling measurements on a number of samples, we will report here results from only two samples. Sample A was polycrystalline single-phase $YBa_2Cu_3O_{9-y}$, and had a resistive transition about 1.3 K wide (10%–90%) with the midpoint of the transition at 92 K [Fig. 1(a)].[20] Sample B was a single crystal of size $120 \times 400 \times 370\ \mu m^3$ with the same nominal composition. Sample B was ideal for tunneling because it allowed orientation dependent measurements. Sample A was large enough for infrared measurements. Magnetic-susceptibility measurements for these samples are shown in Fig. 1(b). The samples were cooled in zero applied field to 4.5 K, then a field of 15 Oe (20 Oe for the single crystal) was applied and the magnetization was measured as a function of temperature as the samples were warmed to above the critical temperature, and then cooled to low temperatures. For the polycrystalline sample the diamagnetic shielding was 50% of the theoretical value at low temperatures, and the Meissner effect was 50% of this value. The single-crystal sample displayed essentially full diamagnetic shielding and about a 20% Meissner effect. The superconducting transitions as measured by magnetic susceptibility were at about 87 K for sample A and about 85 K for sample B. The onsets as measured using high-field susceptibility were slightly reduced in temperature compared with other techniques.[19] Susceptibility measurements of Sample A at 0.01 Oe gave a T_c of 92 K, in good agreement with the resistivity measurements in Fig. 1(a).[20] We have been unable to make measurements of the resistive transitions in our single-crystal samples to date. We take the conservative values from high-field magnetic susceptibility for T_c in our calculations of $2\Delta/k_BT_c$ below. Our qualitative conclusions do not depend on the exact choice of T_c.

The tunneling current-voltage characteristics were measured using a PtIr tip in a low-temperature scanning

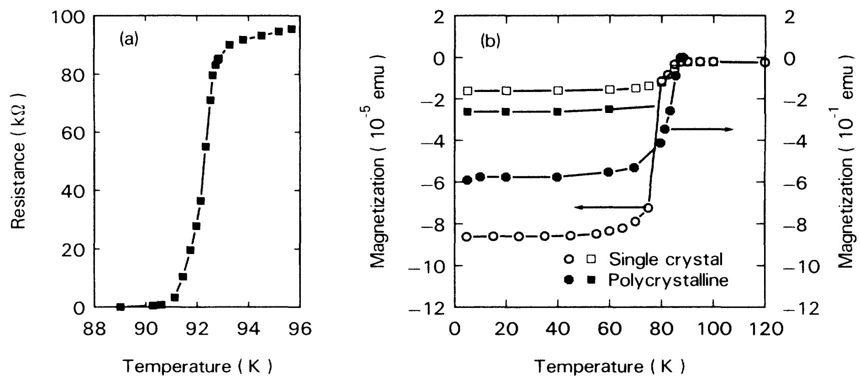

FIG. 1. (a) Resistive transition for the polycrystalline single-phase sample A, and (b) magnetic-susceptibility measurements for the polycrystalline single-phase sample A and the single-crystal sample B. In (b) the circles were taken while warming the sample and the squares were taken in the subsequent cooldown.

tunneling microscope. The microscope design and operation have been described elsewhere.[22] The Y-Ba-Cu-O samples behaved in the tunneling microscope very much like the La-Sr-Cu-O samples described previously.[11] The tunneling current-voltage and current-spacing characteristics were consistent with vacuum tunneling at high tip voltages, but the tip had to be driven deeply into the sample to obtain measurable tunneling currents at low voltages. This made it impossible to scan the tip with respect to the surface to obtain the spatial dependence of the energy gap. A dynamic conductance-voltage characteristic for tunneling into the single-crystal sample B with the tunneling tip oriented perpendicular to the CuO planes is shown as the solid line in Fig. 2(a). These data were obtained using standard voltage modulation techniques. As with $La_{2-x}Sr_xCuO_4$ samples,[11] the tunneling results varied significantly from approach to approach, possibly because of spatial inhomogeneities in the material, particularly near the surface. Our tunneling measurements of sample A (and several other Y-Ba-Cu-O samples) showed gap energies comparable to those obtained from sample B, but gave lower quality tunneling characteristics.

Although the conductance-voltage characteristic of Fig. 2(a) shows the minimum in conductance at zero bias and the "overshoot" due to the singularity in the density of states at the gap edge characteristic of superconductivity, it is far from ideal. For comparison, the prediction of standard tunneling theory for a planar superconducting/insulator/normal-metal junction, with a superconducting BCS density of states, $\Delta = 18$ meV, and a temperature of 5 K, is shown as the dashed curve. The experimental curve shows excess conductance at zero bias, asymmetry in the two opposite sweep directions, a background conductance that rises nearly linearly with voltage, and large additional structure at voltages higher than the gap voltage. The additional structure appeared as evenly spaced peaks that occasionally had quite dramatic intensities. Similar observations were made for tunneling into La-Sr-Cu-O.[11] We were unable to fit the linear dependence of conductance on voltage with standard tunneling theory using, for example, low effective tunneling barrier potentials. On the other hand, the linear dependence of conduc-

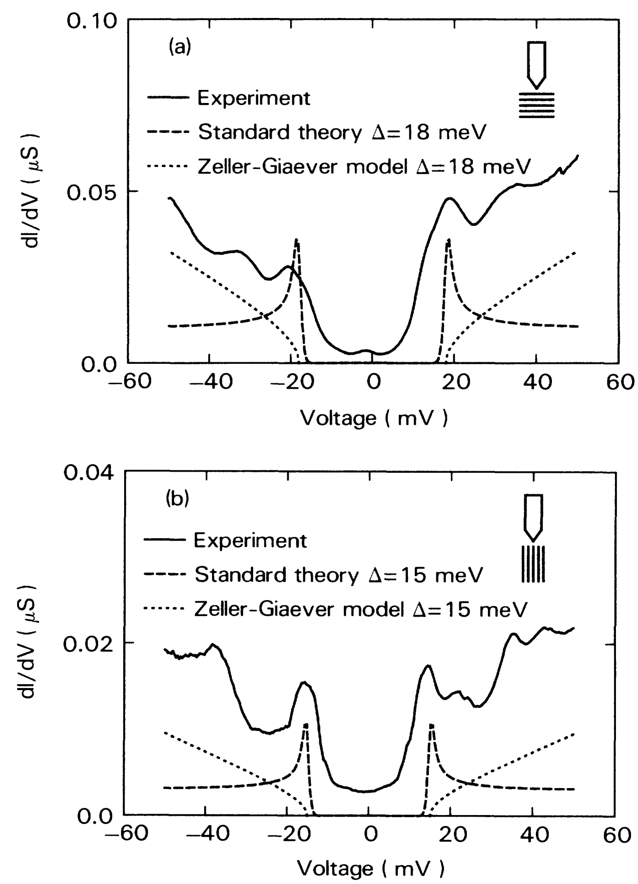

FIG. 2. Conductance-voltage characteristic for tunneling from a PtIr tip into the single-crystal $YBa_2Cu_3O_{9-y}$ sample B. The data were taken with the tip approaching the sample (a) perpendicular to the CuO planes and (b) parallel to these planes. The dashed lines are the predictions for standard tunneling theory for planar superconducting/insulator/normal-metal tunnel junctions using a BCS density of states with an energy gap $\Delta = 18$ meV (a) and 15 meV (b), respectively, and a temperature of 5 K. The dotted curves are the prediction of the model of Zeller and Giaever for tunneling into a granular superconductor, in the limit of small interparticle capacitances.

tance on voltage is consistent with the Zeller-Giaever model for tunneling into granular superconductors,[23] but only if we assume that tunneling occurs at least partially into isolated superconducting regions with sufficiently small intergrain capacitance C that the inequality $e/C \gg \Delta$ is satisfied. As discussed previously,[11] this would imply that isolated superconducting regions of 100-Å-diam size are present, even in this single-crystal sample. This is reminiscent of the conclusions of Müller *et al.* from measurements of susceptibility and magnetic moment in La-Ba-Cu-O samples.[17] They infer the existence of a superconducting glass state in some of their samples, with homogeneous superconducting areas smaller than 0.03 μm^2. The dotted curve in Fig. 2 represents the prediction of the model of Zeller and Giaever in the limits $T=0$, $e/C \gg \Delta$, with a BCS superconducting density of states with $\Delta = 18$ meV. The model of Zeller and Giaever reduces to standard tunneling theory (dashed curve) in the limit of large interparticle capacitances (large regions). The experimental conductance-voltage curve appears to be composed of a combination of the curves expected for large regions (dashed curve) and small regions (dotted curve).

It is difficult to assign a gap value to the data of Fig. 2(a) in the absence of a detailed model for the conductance-voltage behavior in this very complex system. Nevertheless, limits on the gap value can be placed. By comparison with the predictions of the standard tunneling model with a BCS density of states, the gap (2Δ) should be smaller than the potential difference between the two peaks in conductance (corresponding to $\Delta < 19.4$ meV), but larger than the potential difference between the conductance peaks at half the peak height (corresponding to $\Delta > 12.6$ meV). These two limits correspond to $5.3 > 2\Delta/k_B T_c > 3.4$, if we take $T_c = 85$ K. The lower limit is comparable to the BCS prediction of $2\Delta/k_B T_c = 3.53$, and the upper limit is larger than observed for previously studied strong coupling superconductors such as Pb or Hg,[24] and would correspond to a coupling strength $\lambda \sim 2.5$ (for $\mu^* = 0.1$).[25]

A tunneling conductance-voltage characteristic taken with the tip oriented parallel to the CuO planes is shown in Fig. 2(b). This is the largest and most well-defined gap observed from many measurements for this orientation. The data shown in Fig. 2(b) have a slightly smaller gap than for Fig. 2(a), and the additional structure above the gap voltage is more pronounced, but these differences are within the variations observed from approach to approach for the same tip orientation, so that we can report no significant differences in the observed gaps for tunneling using the two different tip orientations. This is not surprising, since we had to drive the tip deeply into the sample in both cases to get tunneling currents at low tip-sample biases.

Infrared reflectivity of nominally unpolarized radiation incident at $\sim 45°$ was obtained with a scanning Fourier transform interferometer. In Fig. 3 (solid line) we show the ratio of the reflectivity in the superconducting state ($T = 13$ K) to that in the normal state ($T = 93$ K) for sample A. The dashed curve in Fig. 3 shows the ratio of two separate runs taken at 93 K. The deviation of this ratio from 1 gives an indication of the noise, drift, and extra structure due to beam splitters and windows in this experiment. Below the gap frequency the reflectivity of the superconducting state is higher than that in the normal state, as expected, but above 200 cm^{-1} the ratio drops below 1 due to extra absorption in the superconducting state, although the dip is not nearly as pronounced as in $La_{2-x}Sr_xCuO_4$.[26] In addition, in all of the single-phase samples of Y-Ba-Cu-O that we have measured we have seen additional structure in the gap, due to infrared-active optic-phonon modes. Because of the complex nature of this data it is difficult to assign a gap value. By comparison with the Mattis-Bardeen theory[27] a lower limit for the gap may be set by the energy at which the reflectivity ratio starts to drop (~ 100 cm^{-1}). A reasonable upper limit is set by the energy at which the ratio crosses one (~ 215 cm^{-1}). These two limits correspond to 6.2 meV $< \Delta < 13.3$ meV, or $1.6 < 2\Delta/k_B T_c < 3.4$, taking $T_c = 87$ K as discussed above.

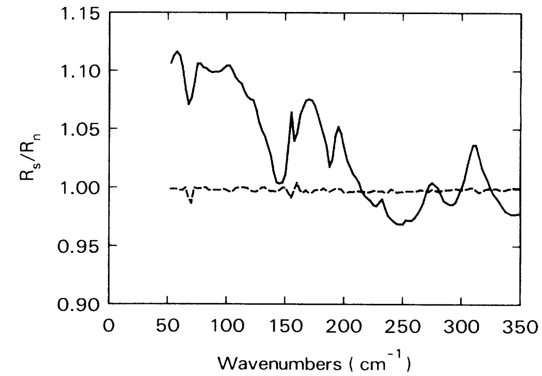

FIG. 3. We show the normalized reflectance R_s/R_n between the superconducting (13 K) and normal (93 K) states of the Y-Ba-Cu-O composition sample A as a function of frequency (solid line). Also shown is the reflectivity ratio for two runs taken at 93 K (dashed curve).

The energy gaps measured using tunneling are significant because they show that this superconducting property of the high-critical-temperature Y-Ba-Cu-O phase fits into standard theory, despite the fact that this material has a transition temperature that would have been unthinkable only a few months ago. Our tunneling results are typically much higher than the infrared results. The reduced infrared gap is probably due in part to the fact that the gap extends into the energy range of the optic phonons. The electronic and phonon contributions to the reflectivity could tend to depress the ratio in Fig. 3 at higher frequencies, causing an underestimate of the gap. Small differences between energy gaps of more conventional superconductors measured using infrared and tunneling have been noted before, especially for strong-coupling superconductors. These differences have sometimes been attributed to poor surface conditions.[28] Another possible explanation is that the infrared averages over a relatively large volume of material compared with tunneling from a sharp tip. If there were spatial inhomogeneities or anisotropies in the gap, this averaging would tend to lower the infrared value compared to the tunneling value, since we only report the largest and sharpest gaps obtained from many tunneling measurements. However, it is difficult to see how these effects could cause the observed differences, especially since modeling using the theory of Mattis and Bardeen[27] shows that volume-averaging effects tend to smear out the structure at the gap edge, rather than lowering the apparent gap energy. A third, more speculative, explanation for these results is that there is a distribution of energy gaps in these samples, and that the infrared measurements are less sensitive to the high-energy gaps than the tunneling measurements.[29] More experiments with single-phase Y-Ba-Cu-O samples may help to resolve some of these questions.

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