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Local tunneling measurements of the high-T_c superconductor $La_{2-x}Sr_xCuO_{4-y}$

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We have measured the current-voltage (I-V) characteristics for tunneling into the superconducting layered copper oxide $La_{2-x}Sr_xCuO_{4-y}$ using a low-temperature scanning-tunneling microscope. The I-V curves were highly nonlinear, even at low voltages, with evidence for superconducting energy gaps Δ of several meV. Substantial variation of Δ was observed from measurement to measurement, with the largest being $\Delta \sim 7$ meV, corresponding to $2\Delta/k_BT_c \sim 4.5$.

Since the discovery of high-temperature superconductivity in the layered copper oxides by Bednorz and Müller,[1] there have been several reports[2-4] of superconductivity in this new class of oxides with T_c's in the temperature range of 40–90 K. To obtain insight into the fundamental nature of the observed high-temperature superconductivity, a number of experimental tools have already been used to study these new superconducting compounds, including transport, magnetic susceptibility, low-temperature x-ray crystallography, calorimetry, and far-infrared transmission and reflectance.[5-8] In particular, the infrared transmission and reflectance measurements[9] have indicated that a superconducting gap Δ with a wide distribution (presumably due to spatial inhomogeneity) centered at about 3 meV exists in a high-T_c $La_{2-x}Sr_xCuO_{4-y}$ superconductor (where y represents an undetermined amount of oxygen deficiency).

Tunneling spectroscopy has traditionally been an important tool for the study of superconductivity. Tunneling measurements provide not only a direct measure of the superconducting energy gap and the phonon density of states, but also of the electron-phonon coupling strength, which plays a crucial role in the mechanism of superconductivity. We have tunneled into high transition temperature $La_{2-x}Sr_xCuO_{4-y}$ using a low-temperature scanning-tunneling microscope (LTSTM).[10] The LTSTM is potentially more powerful than infrared techniques for studying inhomogeneous superconducting systems because of its spatial resolution. Our tunneling current-voltage characteristics were very nonlinear, even at voltages of a few tens of meV's. The tunneling dynamic conductance, rather than the tunneling current, varied nearly linearly with voltage up to 100 meV. Moreover, there was evidence for a superconducting energy gap. There were very small currents for voltage biases within a few millivolts of zero, and occasionally overshoots in the conductance versus voltage characteristic resulting from the divergence in the density of states at the gap edge. These results were consistent with the Zeller-Giaever model for tunneling into a granular superconductor,[11] but only if we assumed that spatial inhomogeneities much smaller than the grain sizes were present in the samples. Fits to this model gave energy gaps that varied substantially from approach to approach. The largest observed gap was about 7 meV. This value is larger than would be expected from the BCS relation $\Delta = 1.76k_BT = 5.5$ meV, given the observed critical temperature of 36 K (midpoint of the resistive transition), but comparable to that found in strong coupling superconductors. The large variation in gaps from measurement to measurement was consistent with spatial inhomogeneities in the material.

The superconducting oxides were prepared in two ways, by reacting the oxides at temperatures of 1050 °C (sample a), and from nitrate solutions which were subsequently converted to the oxides and sintered at 1180 °C (sample b). The latter procedure produced single phase materials with larger grains, i.e., sizes up to 30–50 μm. Sample a had a nominal Sr composition $x = 0.2$ and sample b had an analyzed Sr composition of $x = 0.15$. Resistance measurements of sample a after aging for a few days (Fig. 1), showed a superconducting transition with an onset at about 40 K, with completion at 33 K. Superconducting quantum interference device magnetometer measurements showed about 35% Meissner effect. The magnetic measurements based on the Meissner effect also indicated that the majority (80%) of the superconducting transition took place in the temperature range of 35–25 K. The resistive transition for sample b was similar to that for sample a.

The scanning-tunneling microscope used in this study was a single segmented piezotube, differential spring approach microscope[12] designed to work in the He^3 space of

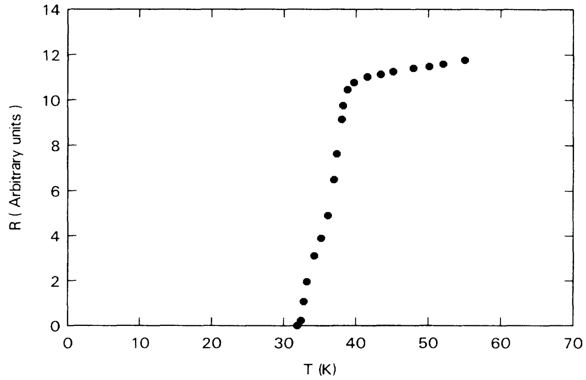

FIG. 1. Resistance vs temperature for a sample of $La_{1.8}Sr_{0.2}CuO_{4-y}$ (sample a), from the same batch as that used for the tunneling measurements. The measuring current density was 0.01 A/cm^2.

a single shot He^3 refrigerator, which was in turn in the bore of an 8 T superconducting magnet. Further details of the microscope design and operation will be reported elsewhere.[13] With this microscope we have obtained high-quality current-voltage characteristics of NbN superconducting films, showing both the surface topology and the spatial variation of the energy gap.[14]

The freshly prepared $La_{2-x}Sr_xCuO_{4-y}$ samples were mounted in the LTSTM with silver paint or low-temperature epoxy; the sample chamber was pumped out to 1×10^{-6} Torr with a turbomolecular pump, and cooled to 5 K in the presence of 2 mm of He_4 exchange gas. Once the sample was cold an approach was made with the tunneling tip. The z-piezo of the STM was used to keep the tunneling current constant at 1 nA in feedback mode. At tip voltages above a few volts, the tip-sample current had the characteristics of vacuum tunneling. There was a high effective barrier evident in both the current-voltage and current-spacing characteristics. However, at lower tip biases the current was a very insensitive function of the z-piezo voltage, and the current-voltage characteristics were nonlinear even at very low voltages. Attempts to measure the surface topography at low voltages were unsuccessful, showing large hysteresis in the z-piezo voltage with opposite horizontal tip sweep directions. We interpreted these results to mean that at low voltages the tunneling was not through vacuum, but instead through a semi-insulating layer at the surface of the $La_{2-x}Sr_xCuO_{4-y}$.

Nevertheless, we were able to obtain characteristics of the tip-sample current by briefly interrupting the feedback loop, sweeping the tip voltage, and measuring the tunneling current. One such current-voltage characteristic for tunneling from a Pt-Rh tip into sample a at $T=5$ K is shown in Fig. 2. As can be seen, there was large curvature in the characteristic, even at voltages below 50 mV. We were not successful in modeling the current-voltage characteristics with standard tunneling theory using a trapezoidal tunneling barrier. To be specific, model barriers which fit the observed curvature at high voltages were not nonlinear enough at low voltages; on the other hand, predicted curves for model barriers which fit the observed curvature at low voltages varied too rapidly at high voltages.

The tunneling characteristics were very nearly linear when plotted as dynamic conductance versus voltage over all but the smallest voltages. The model of Zeller and Giaever for tunneling into granular superconductors[11] predicts such a linear dependence. This model treats tunneling from a bulk electrode (in our case the tunneling tip) into a system of small superconducting grains separated by insulating material. For this model to be applicable for our experiments we must assume that electrons tunneled from our tip into many superconducting grains. (The granularity of the sample is supported by the structure in the resistive transition shown in Fig. 1.[15]) We must therefore postulate that inhomogeneities provide granularity on a scale much smaller than the individual crystallites visible in scanning electron microscope images of these samples, which were a few microns in diameter. If the grains were sufficiently small, and had sufficiently small intergrain capacitance C, there would exist a "Coulomb gap" in the conductivity as a function of voltage with width e/C displaced from zero bias by a voltage V_D, where V_D is the voltage difference between the lowest empty grain energy level and the tunneling tip Fermi level. In the limits where (1) the tunneling barrier between the tip and the particles was much larger than that between the particles, (2) the bias voltage $|V|<e/C$, (3) a uniform distribution for V_D in the particles is taken, and (4) $k_BT\ll\Delta$; this model predicts a current-voltage characteristic given by

$$I(V)=\pm k\left[\frac{|eV|}{2}\sqrt{(eV)^2-\Delta^2}-\frac{\Delta^2}{2}\cosh^{-1}(|eV|/\Delta)\right], \qquad (1)$$

where k is a constant, and the positive (negative) sign is taken for positive (negative) voltages.

The dashed line in Fig. 2 shows the best fit of Eq. (1) to

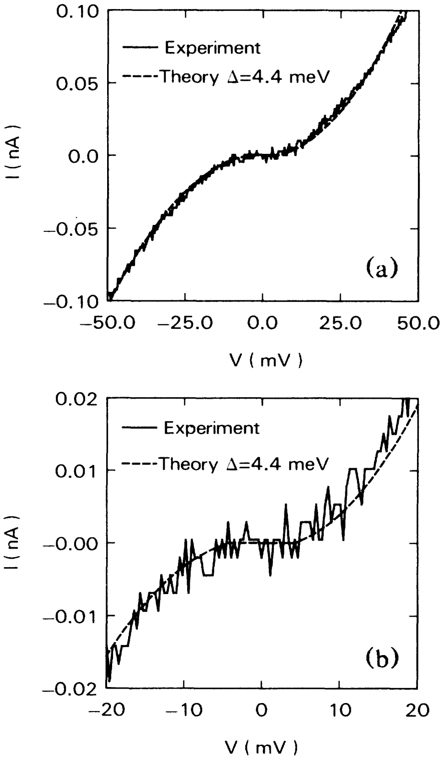

FIG. 2. Current-voltage characteristics for tunneling from a PtRh tip into a sample of $La_{1.8}Sr_{0.2}CuO_{4-y}$ (sample a) at a temperature of 5 K. The solid curve is experiment and the dashed curve is a fit to the theory of Zeller and Giaever using the superconducting energy gap as a fitting parameter. The best fit value was $\Delta=4.4$ meV. (b) has the same data as (a) on an expanded scale. The noise in (b) is dominated by "bit" noise, caused by the limited dynamic range of our analogue-digital converter. The tunneling current was controlled by feeding back on the z-piezo drive at 0.5 nA at a tip bias of 100 mV, before the feedback circuit was interrupted briefly to obtain the current-voltage characteristic.

the experimental curve. Since there was a slight asymmetry in the I-V's with opposite bias directions, we used three fitting parameters, two k's for the two bias directions, and the energy gap Δ. The best fit for the data of Fig. 2 gives an energy gap of 4.4 meV. The tunneling resistance between the tip and the sample tended to be unstable for periods longer than a few minutes, much more so than with samples that showed clear vacuum tunneling characteristics such as Au or NbN. We therefore had to periodically readjust the mechanical spacing in the STM. Each time we readjusted the spacing, the new current-voltage characteristic tended to be slightly different from the last. We speculate that our tip, identical in preparation to one which resolved surface features and spatial variations in the superconducting energy gap on the scale of a few tens of angstroms in NbN, was tunneling into slightly different areas in the sample with each readjustment, giving different results.

In the analysis of our data above, we assumed that e/C was larger than 100 mV. This limit is justified experimentally, since the saturation of the linear dependence of dynamic conductance on voltage predicted by the model of Giaever and Zeller should occur for voltages larger than e/C, and no such saturation is seen up to 100 mV. If e/C is greater than 100 mV, then the intergrain capacitances C are less than 2×10^{-18} F. If we assume that the intergrain tunneling barriers are 15 Å thick, and take a dielectric constant of 10, this would imply intergrain surface areas of 3×10^{-13} cm^2, corresponding to, for example, disk-shaped particles of diameter 60 Å, much smaller than the microcrystallite sizes observed in scanning electron microscopy (SEM) images of this material. The success of the Zeller-Giaever model in modeling our results implies that the tunneling is controlled by spatial variations on a much smaller scale than are apparent in the SEM images.[16] If true, this is an important clue to the remarkable properties of these materials.

Occasionally, we also saw clear indications of the characteristic "overshoot" in the conductance versus voltage characteristic arising from the divergence in the BCS density of states at the gap edge. Such a conductance-voltage characteristic, taken with sample b using a PtIr tunneling tip, is shown in Fig. 3. For comparison, the dashed curve is the theoretical prediction for tunneling in planar normal-metal–insulator-superconductor junctions, using the BCS density of states with an energy gap of 7 meV and a temperature of 5 K. The experimental conductance rises strongly outside the gap region, and the characteristic is asymmetrical, but there are clear indications of the gap edges. Note that the characteristic in Fig. 3 is inconsistent with Eq. (1), which was derived in the limit of small interparticle capacitances. The experimental conductance in Fig. 3, in fact, looks more like what might be expected for tunneling into a bulk sample with a large spatial variation in the energy gap. We speculate that this type of conductance-voltage characteristic occurs when we tunnel into larger superconducting grains. This would give less smearing of the superconducting gap by Coulomb effects. It is difficult to assign an exact value to the gap in the measurement of Fig. 3 in the absence of detailed modeling. However, some limits can be placed. The conductance-voltage characteristics generated using the BCS density of states show that the potential difference between the two conductance peaks at their maxima is larger than 2Δ (corresponding to $\Delta < 9.7$ meV for the data of Fig. 3), but that the potential difference between the two conductance peaks at half their maxima is smaller than 2Δ (corresponding to $\Delta > 5.5$ meV). These two limits would correspond to a range in $2\Delta/k_BT_c$ of 3.5–6.3 if we use $T_c = 36$ K (the midpoint of the resistive transition). The lower limit is comparable to the BCS prediction of 3.53 and the upper limit is larger than those commonly reported for strong-coupling superconductors.[17]

It is interesting to note the apparent discrepancy between our tunneling measurements of the superconducting energy gap and infrared measurements. Schlesinger measured the energy gap of sample b using infrared reflectance as $\Delta \sim 3$ meV,[18] while we observe gaps larger than 5.5 meV. There are two possible explanations for this discrepancy. The first is that superconducting energy-gap values obtained using infrared techniques are sometimes lower than those obtained using tunneling. This difference has been attributed to poor surface conditions.[19] The second explanation is that infrared reflectance averages over a larger volume of the sample than tunneling. We see a large variation in the observed gaps from measurement to measurement, and report here only the largest gaps observed.

Tunneling with a local probe shows promise for studying the properties of high critical-temperature superconducting oxides, especially if samples can be prepared in such a way that scanning is possible. In particular, it would be very interesting to study the effective density of states above the gap energy to obtain the phonon state densities and coupling constants.

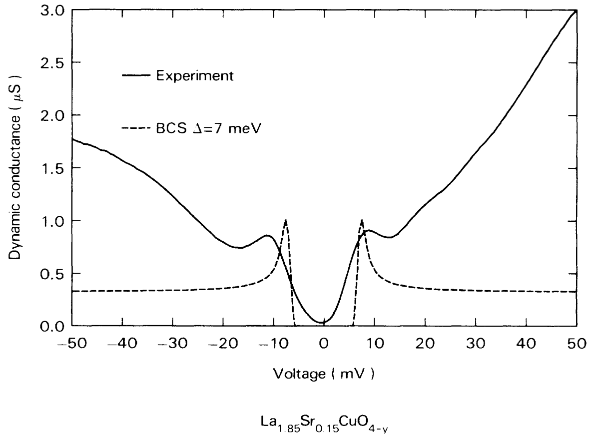

FIG. 3. Dynamic conductance vs voltage for tunneling from a PtIr tip into a sample of $La_{1.85}Sr_{0.15}CuO_{4-y}$ (sample b) at $T = 5$ K. The dashed curve is the standard theoretical prediction using $T = 5$ K and a BCS density of states with $\Delta = 7$ meV. The experimental data were obtained using standard voltage modulation techniques with a voltage modulation amplitude of 1 mV rms and a modulation frequency of 520 Hz.

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