RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 13 1 MAY 1987

Energy gap in $La_{1.85}Sr_{0.15}CuO_{4-y}$ from point-contact tunneling

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(Received 27 February 1987)

Point-contact tunneling into the high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_{4-y}$ reveals the first direct measure of the energy gap. Values range from 8 to 14 meV with the variation perhaps due to impurity phases, pressure-induced changes, or anisotropy. Even the minimum value indicates a strong-coupling superconductor.

The extremely high transition temperature T_c found recently[1,2] in the perovskite oxides, e.g., $La_{2-x}Sr_xCuO_{4-y}$ have lead to speculation about possible new, nonphononic mechanisms[3] providing the superconducting interaction. On the other hand, several authors[2,4,5] have suggested that the results are consistent with the usual phonon-mediated attractive electron-electron interaction. Electron tunneling provides two pieces of information which can shed light on this question: The energy gap Δ and the electron-phonon spectral function $\alpha^2F(\omega)$, where $F(\omega)$ is the phonon density of states. For the case of the usual phonon-mediated superconductivity, high T_c has been predicted to result from the Cu-O_I breathing modes since they couple strongly to the conduction-electron wave functions which involve orbitals of these two atoms. In one variation of this model[2] the high frequency of these modes results in a large prefactor in the T_c equation, thus requiring only modest values of electron-phonon coupling. A second possibility involves the frequency of these modes renormalized to much smaller values by the very strong electron-phonon coupling.[5] Measurements of the energy gap, compared to k_BT_c, are a good indicator of strong coupling.

We report point-contact tunneling measurements on a polycrystalline, bulk sample with $x=0.15$, and infer that the material is very strong coupling, with $2\Delta(0)/k_BT_c \gtrsim 5.2$, compared to the weak-coupling BCS limit of 3.53. Values of the gap, smaller than the BCS limit, have been recently reported from infrared reflection and transmission experiments;[6,7] however, several of these authors state[6] that this is only a lower limit due to the possibility of proximity effects with nonsuperconducting or lower T_c impurity phases. Because of the very high resistances of our point-contact junctions, we feel that tunneling is most likely spatially localized, as in vacuum tunneling, and less likely to average out large and small gaps.

The sample was prepared using a coprecipitation technique followed by pressing and sintering. In this technique the soluble nitrates of La, Cu, and Sr are mixed in solution in their correct proportions. After thorough mixing the materials are coprecipitated as insoluble oxycarbonates through the addition of sodium carbonate. The precipitate is filtered and washed until the pH of the rinse solution is neutral, then dried overnight in a 140 °C drying oven. The dried oxycarbonate powder mixtures are then fired at 825 °C for 2 h to decompose the carbonates into oxides. The 2θ x-ray diffraction patterns clearly show the formation of the tetragonal phase even at this low temperature, indicating the high degree of intimate mixing achieved with this technique. The oxide powders are then pressed using a $\frac{3}{8}$-in. die to approximately 60% of the theoretical density, sintered at 1100 °C in air for 4 h, then quenched in air. The resulting pellets are generally about 80% of the theoretical density of 7.14 g/cc. Resistivity samples are cut from the pellets using a diamond-wire saw. The pellets are then annealed in flowing O_2 for 12 h at 475 °C.

The transition temperature of a piece of the sample used for point-contact tunneling has been determined using a four-probe dc resistance measurement with a sample current of 1 nA. The midpoint of the resistive transition is at 35.9 K with a transition width of 2.5 K (10–90% of resistive transition). The sample exhibits zero resistance below 32 K.

The tunneling apparatus is described in detail, together with a discussion of tests done on conventional superconductors and the interpretation of point-contact tunneling, in a study of an organic superconductor in Ref. 8. In that case,[8] as well as here, an insulating surface layer prevented true vacuum tunneling and the soft Au tip had to be pushed into the surface of the sample to obtain a measurable current. However, the present material resulted in more stable and easily repeatable junctions than the organics.[8]

Figure 1 shows an $I(V)$ curve taken at 4.2 K on the perovskite oxide with $x=0.15$. Although a high-resistance region representing the energy gap is readily discerned, there are differences with the ideal $I(V)$ curve for tunneling between a normal metal and a superconductor.[9] There is an asymmetry in $I(V)$, and at higher voltages the conductance begins to rise. Such tunneling effects are well known[10] and can result from (a) a low tunneling barrier height (energy) compared to eV, and (b) dissimilar electrodes. At liquid-nitrogen temperature we find smaller conductance increases at high voltages, but little or no asymmetry and no other structure in the $I(V)$. In all figures, the positive voltage means the perovskite sample is positive with respect to the Au tip. These effects vary with the location of the tip and its contact force, and the data shown have been selected to minimize them.

The standard analysis[8] of such low-temperature ($T \ll T_c$) data for a junction between a normal metal and superconductor is to fit to the BCS expression $RI(V)=(V^2-\Delta^2)^{1/2}$, where R is the high-voltage

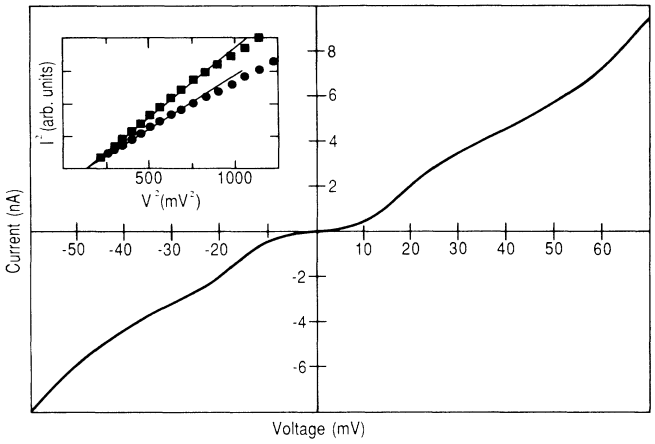

FIG. 1. Point-contact tunneling $I(V)$ between a gold tip and a polycrystal sample of $La_{1.85}Sr_{0.15}CuO_{4-y}$. Inset: I^2 is plotted vs V^2. For ideal tunnel junctions between a normal metal and BCS superconductor, the slope is R^{-2} and intercept is $(\Delta/e)^2$. The straight line fits give $\Delta \sim 11$ meV.

$(V \gg \Delta)$ junction resistance. Unfortunately, convincing fits were impossible using the same R for both polarities. Plots of I^2 vs V^2 are shown in the inset of Fig. 1. Using different R values led to an extrapolated value of $\Delta \sim 11$ meV for each polarity.

Figure 2 shows another $I(V)$ curve which was obtained by readjusting the force on the tip, and thus potentially changing the precise tunneling position on the sample. Although a high-resistance region representing an energy gap of 8–9 meV is still readily discerned, the polarity asymmetry is more pronounced, especially at high voltages, and there appears to be additional structure in the form of bumps or dips. Figure 3 shows the voltage derivative of $I(V)$ for another tip position. The asymmetric, parabolic background conductance is clearly visible together with a well-defined single gap. We estimate Δ to be 8 meV, using the intercepts of the curve with a reasonable guess for the background conductance. The conductance minimum is about 50% of the extrapolated background. Note that in Figs. 1 and 2 the leakage conductance is less than 10%.

The differences in measured gap at various locations could be due to inhomogeneities in the sample (higher or lower T_c), proximity effects[11] with lower T_c impurities, pressure-induced increases in T_c (and hence Δ) due to the tip, and/or intrinsic gap anisotropy.[8] However, no evidence has been seen for the very small gap reported in infrared measurements.[6,7]

Using an energy gap of 8.5 meV, we have drawn in Fig. 2 the ideal $I(V)$ curve, first by matching the high-voltage R in the positive quadrant (long dashed line) and second by matching the region between 9 and 14 meV (short dashed line). The bumps or dips in Fig. 2 were not always found in cases where clear gap structure can be seen (see Fig. 1); however, similar bumps or dips were repeatable after removing, breaking, and remounting the same sample. These could result from inelastic tunneling via states in the barrier, such as those studied extensively by others.[12] However, to be visible on the $I(V)$ curve they would represent a considerably greater effect (times 50) than previously reported. On the other hand, these structures could result from very strong-coupling to low-lying phonon modes.[13] However, again the magnitude would be about six times greater than the most strongly coupled su-

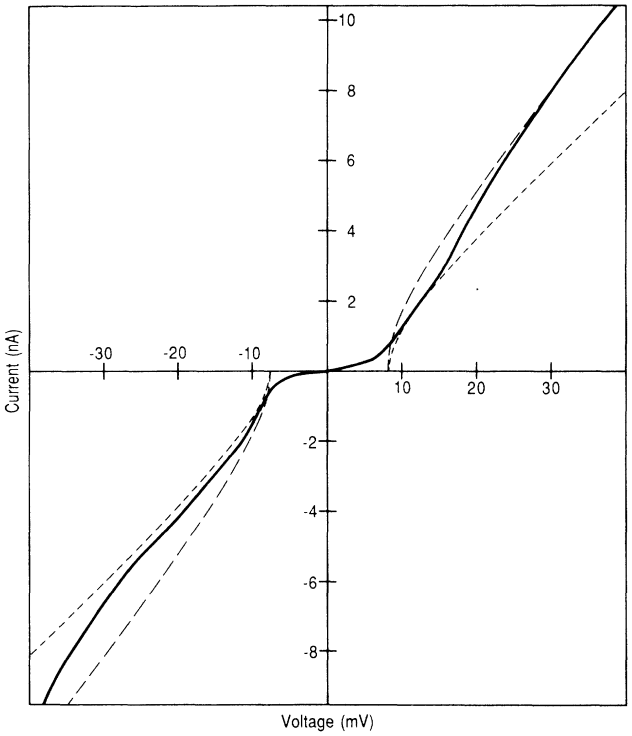

FIG. 2. Another $I(V)$ for a different location on the same sample (solid line). Using $\Delta = 8.5$ meV the other curves represent the BCS prediction by fitting (for positive voltages) to the high-voltage resistance (long dashed curve) and to the current between 10 and 14 meV (short dashed line).

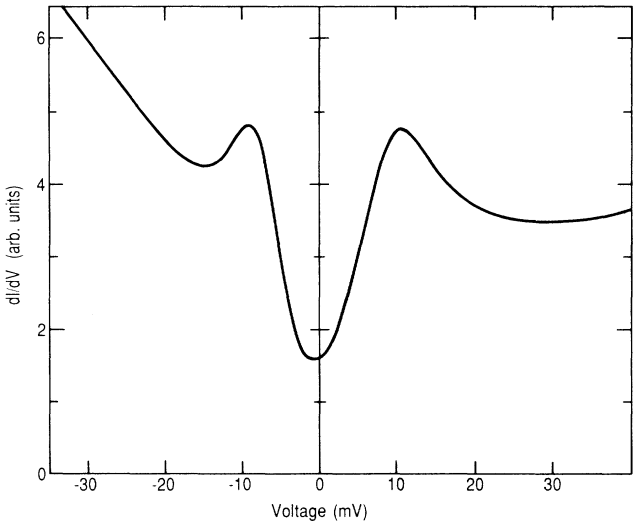

FIG. 3. Plot of dI/dV for another location on the sample. The intersection of this curve with a guessed, smoothly curving background gives $\Delta \sim 8$ meV.

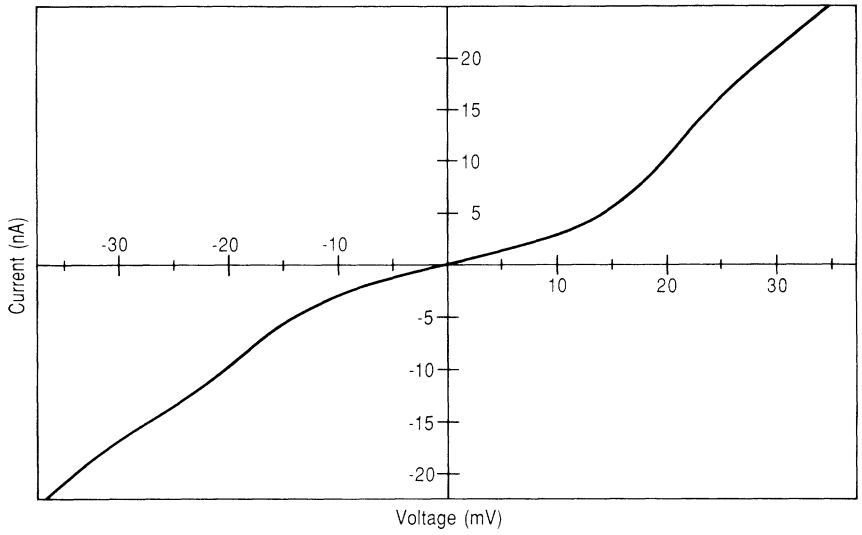

FIG. 4. Another $I(V)$ obtained at yet another position on the polycrystal sample. Here, only a larger gap of ~ 14 meV is found.

perconductors measured to date (i.e., in Pb, phonons result in conductance changes of $\sim \pm 5\%$). The most convincing demonstration of phonon coupling would be to show, as in the case of many elemental superconductors,[14] a correlation of the $I(V)$ structure with the phonon density of states, e.g., measured by neutron scattering. Unfortunately, such a correlation may be difficult without convincing calculations and/or measurements of the phonon density of states for individual modes as in the case of the $Ba(Pb_{0.75}Bi_{0.25})O_3$ system.[15] Another problem of calculating $\alpha^2F(\omega)$ from point-contact tunneling is the difficulty of measuring the normal state $I(V)$. The critical fields are extremely high,[16] and problems of thermal expansion make measurements at temperatures up to and above T_c very difficult without movement of the tunneling tip.

Finally, this additional structure in Fig. 2 could represent a larger energy gap due to anisotropy or another superconducting phase. The magnitude of current associated with this additional bump exceeded the smaller gap structure for some tip locations and in one case was the only feature visible (Fig. 4). Interpreting Fig. 4, as we did Fig. 1, results in a gap of about 14 meV, whereas the larger gap value in Fig. 2 is likewise about 14 meV. For this additional structure, one cannot rule out more exotic explanations like charge-density waves or even a semiconducting gap from impurity orthorhombic phases.[17]

In summary, the tunneling $I(V)$ result in an energy gap of 8–14 meV, indicating a strong-coupling superconductor, and show additional nonideal structure. At this stage it seems premature to make a definitive conclusion about the additional structure, but it could represent inelastic tunneling with barrier states or strong electron-phonon coupling as well as another larger gap.

Even the minimum measured value of $2\Delta(0)/k_BT_c \approx 5.2$ indicates very strong coupling, but it is not as large as that found in the organic superconductor, β-$(ET)_2AuI_2$, where ET is bis(ethylenedithio)tetrathiafulvalane with chemical formula $C_{10}H_8S_8$. Recently,[18] it was pointed out that the maximum value of $2\Delta(0)/k_BT_c$, which is consistent with electron-phonon coupling in the Eliashberg equation, is about 9.5. Therefore, while the organic results exceed that limit, the present result on the perovskite oxide falls below that limit.

Further research is anticipated to better understand the additional structure, especially to look for electron-phonon coupling through $\alpha^2F(\omega)$. Also, when single crystals become available, anisotropy studies may be undertaken.

The authors would like to thank Pat Roach for invaluable help and advice on the tunneling apparatus and Zenon Sungaila for help in constructing the apparatus. We also thank numerous authors who sent copies of their work prior to publication.

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