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Tunneling spectroscopy of $YBa_2Cu_3O_{6.5+x}$ and $Y_{0.95}Al_{0.05}Ba_2Cu_3O_{6.5+x}$ with use of a scanning-tunneling microscope

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We have made measurements at 4.2 K on the high-T_c superconductor $YBa_2Cu_3O_{6.5+x}$ by electron tunneling using a low-temperature scanning-tunneling microscope. In all the samples studied we observe large variations in the energy gap. We observe a very sharp gap in all the samples with $2\Delta = 5$ meV yielding a value of $2\Delta/k_BT_c = 0.7$, far below the weak-coupling limit. The largest gap we measure has a value of $2\Delta = 95$ meV and indicates an extremely strong coupling value of $2\Delta/k_BT_c = 13$. The large gap may be due to tunneling between a series of superconducting regions within the sample. This possibility and other results are discussed in terms of tunneling into a glassy superconductor.

The discovery of high-temperature superconductivity in the copper oxide perovskites by Bednorz and Müller[1] and subsequent work by Wu *et al.*,[2] have initiated a search for a mechanism of superconductivity in these materials. The question is whether or not the interaction leading to the exceptionally high transition temperatures is electron phonon in origin and whether it can be cast within an Eliashberg formalism.[3]

The vast majority of superconductors have an energy gap of 2Δ in the density of states at the Fermi level E_F. Within the Eliashberg formalism, the energy dependence of the energy-gap function contains detailed information about the interaction giving rise to superconductivity. The strength of the interaction can be expressed in terms of the gap-to-transition temperature for which the lower bound is given by the Bardeen, Cooper, Schrieffer (BCS) weak-coupling limit $2\Delta/k_BT_c$ of 3.53.[4]

In the more common superconductors, tunneling has been an excellent tool in probing the quasiparticle density of states. Measurements of the dynamic conductance, dI/dV as a function of bias can be inverted to obtain the strength and detailed dynamics of the interaction giving rise to superconductivity.[5] In the new high-T_c materials, however, there has been no unanimous agreement on measured energy gaps obtained by electron tunneling or infrared techniques. The majority of tunneling data indicates strong-coupling behavior, but values obtained for Δ differ substantially from group to group. Both Ng *et al.*[6] and Kirk *et al.*[7] find values of Δ as high as 45 meV, while others have reported values up to 23 meV.[8-12] Infrared measurements infer values of $2\Delta/k_BT_c$ between 2.5 and 8.[13-17] Extraction of an energy gap from the ir reflectivity measurements is complicated by the low-energy phonon structure present in these data.

Some of the difference in results can be attributed to spatial inhomogeneities. Spatially, the tunneling measurements provide more local information than do infrared techniques. Point-contact experiments find large variations in Δ for different positions on the surface. Infrared measurements sample a much larger region and average over these variations.

In this paper we present tunneling measurements of the energy gap in the high-T_c material. The data we present are from measurements on three polycrystalline sintered samples. Two of these were $YBa_2Cu_3O_{6.5+x}$ and one was an Al-doped sample in which 5 mol% of the yttrium is replaced by aluminum.[18] All three samples are single phase as determined by x-ray diffraction and have zero-resistance temperatures near 88 K. The 20%–80% resistive transition in all three samples is less than 2 K. The samples mounted in the scanning tunneling microscope (STM) were inside edges of sintered pellets, freshly broken, then mounted and subsequently cooled to 4.2 K.

All measurements were made with a low-temperature STM described in detail elsewhere.[19] This microscope operates in liquid helium. It uses a coarse-adjust screw and a fine-adjust piezoelectric transducer to provide a tip-to-sample separation that gives the desired junction resistance. The tips used were made from 0.010 in. W or Nb wire mechanically ground to a fine point and etched in NaOH.

Attempts to obtain atomic-scale topography proved unsuccessful and at resistances of much less than 10^8 Ω the tip tends to get stuck in some sort of insulting surface layer. All energy-gap measurements are made at resistances of about 10^6 Ω to try and ensure the junction is still in the tunneling regime. At these resistances, the tip is undoubtedly embedded within this nonconducting layer. The fact that we are tunneling with an imbedded tip rather than through a vacuum enhances the junction stability. This tenacious surface layer makes it necessary to use the coarse-adjust screw to back off when we want to study a different spot on the sample surface. As a result we were unable to relate any of the topography, even that obtained at the larger tip separations, with the I-V data.

The gap measurements are made by sweeping the voltage at a frequency of 0.5 Hz. This sweep rate is the fastest possible without hysteresis in our measurement setup. To improve the signal-to-noise ratio dynamic conductance dI/dV measurements were made with an even slower sweep rate. In these measurements, a modulation amplitude of less than 1 mV peak-to-peak at a frequency of 5 KHz was applied across the junction and a series resistor of 1 MΩ. The voltage across the series resistor, which is proportional to the dynamic conductance, was then measured by phase-sensitive detection. Both the *I-V* and the dI/dV data are recorded on a digital storage scope.

In measurements performed at 4.2 K, on all three samples, different behavior is seen at various points on the surface. Some points show no gap at all while elsewhere a range of apparent energy-gap values, 2Δ, are seen. Assuming tunneling between the aluminum-doped sample and the Nb tip, Fig. 1 presents examples of three *I-V* curves which show an energy gap. The apparent gap in (a) of approximately 190 meV is the highest we observed, curve (b) has a value of 60 meV, and curve (c) is an example of a small very sharp gap of approximately 5 meV. The data may also be *S-I-S* tunneling between Josephson-coupled regions within the sample and the resulting curves due to a multiplicity of Δ values. The different possible tunneling mechanisms makes an unambiguous estimate of Δ for each curve difficult.

Curves similar to that in Fig. 1(c) are seen in all three of the samples regardless of whether a Nb or W tip is used. The curve in Fig. 2 is obtained from a freshly broken sample with a W tip. The curve yields the same 5 meV value for the energy gap. Subsequent work using the same Nb wire on Mg and Pb indicates that the Nb tip may not be superconducting at 4.2 K. Considering these facts, it seems unlikely that the small gap is related to the tips and is instead a characteristic of the superconducting samples.

The small 5 meV gap seems to have properties distinctly different from the rest of the gaps. The 5 meV gap appears more "BCS-like" (Fig. 2), having less leakage current inside the gap and a more pronounced overshoot in the dynamic conductance at the gap edge.

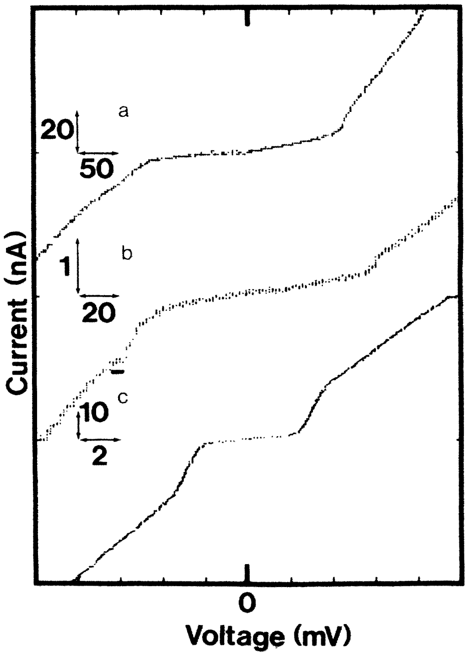

FIG. 1. *I-V* characteristics using a Nb tip at different positions on the surface of the aluminum-doped sample measured at 4.2 K. Note the different scales used for each curve. The spectra show a jump in the current at 95, 30, and 2.5 meV, respectively.

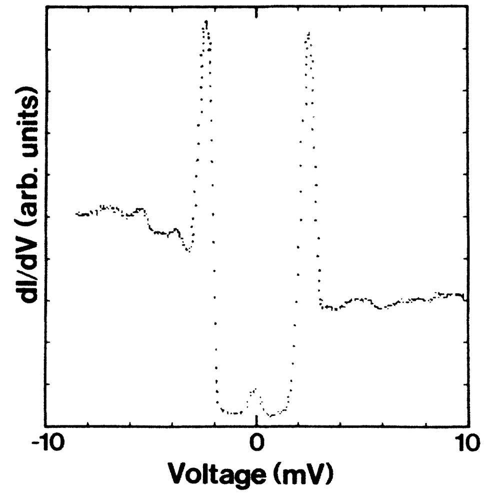

FIG. 2. dI/dV data for $YBa_2Cu_3O_{6.5+x}$ with a W tip measured at 4.2 K.

In general the larger apparent gaps are less stable in time than the smaller gaps. The lack of stability in the larger gaps makes sweeps of dI/dV harder to obtain. The larger gaps are also less defined. The current-voltage characteristics outside the gap are highly asymmetric and have a nonlinear character similar to that seen by other works.[10] The *I-V* characteristics of the smaller gaps are more symmetric with a more linear behavior indicative of tunneling through a higher barrier.

We found no evidence of any gap at 77 K and the spatial variation in the *I-V* characteristics evident at 4.2 K was much less at 77 K.

Evident in Fig. 2, and in much of the dI/dV data, are peaks in the spectra outside the gap region. The positions of the peaks for a point on the surface are stable in time and reproduce over many sweeps. When we tunnel into different points on the surface, curves with similar gap values, in general, show peaks at different energies. The peaks are not symmetric in energy about the Fermi level as one might expect if one were observing electron-phonon interaction-mediated pairing. Is this a manifestation of the absence of electron-hole symmetry? The variation between different points on the surface and the nonsymmetric nature of the peaks, makes an interpretation of the origin of the peaks difficult.

Due to the complicated nature of these materials, the variation in the energy-gap value may have a number of explanations. The samples we measured are polycrystalline and so the different grains are oriented randomly at the surface. The two-dimensional copper oxide planes and the one-dimensional chains give the material an anisotropic character. It may be that grains with different orientations to the surface yield different gap values. This contrasts with measurements on single crystals by Kirtley *et al.*[10] who find an energy-gap value similar in directions perpendicular and parallel to the copper oxide planes.

The variation might also be due to multiple phases within the material. X-ray analysis indicates that all the samples are a single orthorhombic phase. This does not rule out normal phases with the same orthorhombic structure or very small amounts of a different stoichiometry. The insulating surface region may be an example of such a normal region. The only atomic-scale topographs of yttrium barium cuprate at low voltages have been at room temperature.[20,21] The data were undoubtedly obtained in the presence of the same surface layer which makes low-voltage scanning at low temperatures in our samples impossible. The fact that these workers encountered no problems imaging in the presence of this layer indicates that the surface layer may be semiconducting in nature.

Indications are that the range over which variations in the superconducting behavior occur is less than the size of a typical grain. Kirtley *et al.*[10] in their measurements on single crystals, found regions where no gap was present. Other measurements on the same crystals found that incomplete Meissner states could only be explained by normal regions within the crystal.[22] Normal regions may be caused by an excess of oxygen vacancies in different parts of the crystal. These results and others[23,24] indicate that yttrium barium copper oxide is best described as a superconducting glass. The consequences of such a state in these materials has been discussed by Deutscher and Müller.[25] Due to the short coherence lengths, the superconducting state does not extend over small normal regions within the sample. At any point where such a normal region, or even a twin boundary, separates two regions of superconductivity an *S-I-S* tunnel junction would be formed. The macroscopic superconducting properties are then the result of Josephson coupling between microscopic superconducting regions. Josephson coupling between superconducting regions within the sample has been seen with point-contact spectroscopy using normal metal contacts.[24]

The very short coherence lengths will also reduce the value of the gap at surfaces and boundaries with normal phases. In such cases, the measured value of the gap would depend strongly on the region being sampled and the type of interface between the tip and the sample. At temperatures closer to T_c, Deutscher and Müller[25] predict that the value of Δ at interfaces will drop to zero. Such a reduction may explain our results at 77 K.

In the same way as Estève *et al.*[24] ascribed their *I-V* characteristics to coupling between superconducting regions, some of our larger apparent gaps may be due to coupling between two superconducting regions within the sample. In addition, the results of Estève *et al.*[24] also mentioned evidence for coupling between a series of superconducting regions. The extremely large gap values we observe may be due to more than one tunnel junction in series within the sample. Figure 3 shows different gap values for each polarity. It is possible that the rectification and apparent large gap arise from tunneling through a number of tunnel junctions in series, each having a smaller gap. The rectification may be due to Schottky barriers in each of the series junctions. If the current path is different for the two polarities, the coupling between adjacent superconducting regions will, in general, be quite different, and lead to different values in the apparent energy gap on each side. The behavior seen in Fig. 3 is not unique; similar behavior was observed from time to time.

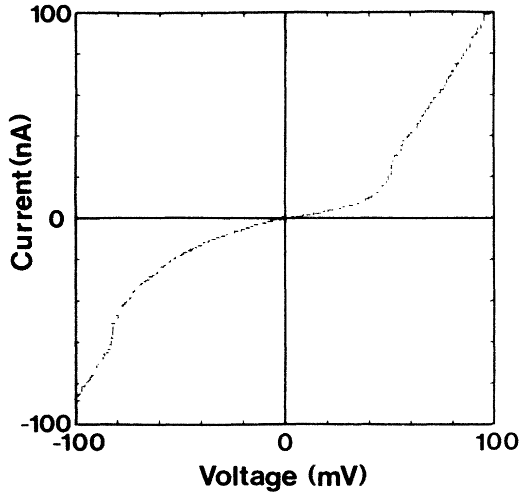

FIG. 3. *I-V* characteristic for the aluminum-doped sample which shows a different value of the apparent gap for each polarity.

A number of sharp small gaps are seen in all three samples. The value of the gap, assuming tunneling between the sample and tip, in all cases was $2\Delta = 5 \pm 0.5$ meV. The variation of 0.5 meV may be due to the spatial inhomogeneities in the samples. The sharpness of the small gaps and the linearity of the *I-V* characteristics outside the gap indicate that the tunneling in these regions is very different from that in the regions where the larger apparent gaps are seen. The dynamic conductance of the small gaps is strongly reminiscent of quasiparticle tunneling in a conventional superconductor.

A value of $2\Delta = 5$ meV and a T_c of 88 K yields $2\Delta/k_BT_c = 0.7$, far below the BCS limit and clearly rules out a BCS-like theory. Since we observe no gaps at 77 K, the possibility of an additional low-temperature phase ($T_c < 88$ K) cannot be rule out.

Tunneling between tip and sample rather than between regions within the sample may yield a larger barrier height. If this is the case, the small gaps and more linear *I-V* characteristics might be indicative of tunneling between sample and tip while the larger gaps may be due to tunneling between superconducting regions separated by low Schottky barriers within the sample.

If indeed the larger gaps are due to *S-I-S* tunneling within the sample, then the apparent jump in current at 95 meV [Fig. 1(a)] could correspond to 2Δ and thus yield a value of $\Delta = 48$ meV. This value assumes the tunneling is between two regions of large Δ and is in agreement with the results of Ng *et al.*[6] and Kirk *et al.*[7] who observed values of $2\Delta/k_BT_c$ as high as 13. If the curve is due to tunneling between a series of superconducting regions then Δ would be even smaller.

In conclusion, we have tried to measure a number of energy gaps in high-temperature copper-oxide superconductors using a low-temperature STM. We find that rather than obtaining one single value, a range of values are found. Two distinct types of gap are found, one with a consistently small value of about 5 meV which is very BCS-like, and a range of larger gaps which are less sharp with asymmetric characteristics. The small gap, although BCS-like, has a value of $2\Delta/k_BT_c=0.7$, far below the BCS weak-coupling limit. The largest gap has a value of $2\Delta/k_BT_c=13$ similar to that found by others; however, our results indicate that this value may be due to tunneling between a series of superconducting regions within the sample. The results are independent of whether we examine the standard yttrium barium cuprate material or one in which the 5% of the Y has been replaced by Al.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] G. M. Eliashberg, Zh. Eksp. Teor. Fiz. **38**, 966 (1960) [Sov. Phys. JETP **11**, 696 (1960)].

[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[5] W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. **14**, 108 (1965).

[6] K. W. Ng, S. Pan, A. L. de Lozanne, A. J. Panson, and J. Talvacchio, in *Proceedings of the Eighteenth International Conference on Low Temperature Physics* [Jpn. J. Appl. Phys. **26**, Suppl. 26-3, 993 (1987)].

[7] M. D. Kirk, D. P. E. Smith, D. B. Mitzi, J. Z. Sun, D. J. Webb, K. Char, M. R. Hahn, M. Naito, B. Oh, M. R. Beasley, T. H. Geballe, R. H. Hammond, A. Kapitulnik, and C. F. Quate, Phys. Rev. B **35**, 8850 (1987).

[8] M. F. Crommie, L. C. Bourne, A. Zettl, Marvin L. Cohen, and A. Stacey, Phys. Rev. B **35**, 8853 (1987).

[9] J. Moreland, J. W. Ekin, L. F. Goodrich, T. E. Capobianco, A. F. Clark, J. Kwo, M. Hong, and S. H. Liou, Phys. Rev. B **35**, 8856 (1987).

[10] J. R. Kirtley, R. T. Collins, Z. Schlesinger, W. J. Gallagher, R. L. Sandstrom, T. R. Dinger, and D. A. Chance, Phys. Rev. B **35**, 8846 (1987).

[11] P. J. M. van Bentum, L. E. C. van de Leemput, L. W. M. Schreurs, P. A. A. Teunissen, and H. van Kempen, Phys. Rev. B **36**, 843 (1987).

[12] A. Barone, A. Di Chiara, G. Peluso, U. Scotti di Uccio, A. M. Cuculo, R. Vagilo, F. C. Matacotta, and E. Olzi, Phys. Rev. B **36**, 7121 (1987).

[13] Z. Schlesinger, R. T. Collins, D. L. Kaiser, and F. Holtzberg, Phys. Rev. Lett. **59**, 1958 (1987).

[14] D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. G. Doss, S. L. Herr, K. Kamarás, and D. B. Tanner, Phys. Rev. Lett. **58**, 2249 (1987).

[15] G. A. Thomas, H. K. Ng, A. J. Millis, R. N. Bhatt, R. J. Cava, E. A. Rietman, D. W. Johnson, Jr., G. P. Epinosa, and J. M. Vanderberg, Phys. Rev. B **36**, 846 (1987).

[16] R. T. Collins, Z. Schlesinger, R. H. Koch, R. B. Laibowitz, T. S. Plaskett, P. Frietas, W. J. Gallagher, R. L. Sandstrom, and T. R. Dinger, Phys. Rev. Lett. **59**, 704 (1987).

[17] J. M. Wrobel, S. Wang, S. Gygax, B. P. Clayman, and L. K. Peterson, Phys. Rev. B **36**, 2368 (1987).

[18] J. P. Franck, J. Jung, and M. A.-K. Mohammed, Phys. Rev. B **36**, 2308 (1987).

[19] J. G. Adler, D. P. Mullin, and M. C. Gallagher (unpublished).

[20] N. J. Zheng, U. Knipping, W. T. Petusky, J. C. Barry, and I. S. T. Tsong (unpublished).

[21] J. E. Klemberg-Sapieha, M. R. Wertheimer, A. Witek, A. Yelon, and A. M. Okoniewski (private communication).

[22] T. R. Dinger, T. K. Worthington, W. J. Gallagher, and R. L. Sandstrom, Phys. Rev. Lett. **58**, 2687 (1987).

[23] K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987).

[24] D. Estève, J. M. Martinis, C. Urbina, M. H. Devoret, G. Collin, P. Monod, M. Ribault, and A. Revcolevschi, Europhys. Lett. **3**, 1237 (1987).

[25] G. Deutscher and K. A. Müller, Phys. Rev. Lett. **59**, 1745 (1987).