Features of the Density of States of High-T_c Superconductors Probed by Vacuum Tunneling

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A scanning tunneling microscope has been used to study $Bi_2Sr_2CaCu_2O_x$ single crystals with transition temperatures of 85 K. Images of atoms and topographical features were obtained at low temperatures and spectra were acquired in the vacuum tunneling mode. Interpretations of the conductance data suggest that $2\Delta/k_BT_c \approx 8.2$. Most significantly, an additional conductance peak at 90 meV, suggesting a localized state, is observed. The latter would appear to support the marginal-Fermi-liquid picture.

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Tunneling measurements can provide critical data for the elucidation of the microscopic mechanism responsible for superconductivity. For this reason, an uncountable number of studies have been performed on high-T_c cuprate superconductors [1]. In principle, tunneling can reveal far more than the energy gap, which has been the focus of most studies, in that density-of-states measurements can yield spectral functions central to the microscopic theory. However, the promise of tunneling has not been generally realized, as for any given material there have been a wide range of values reported for the magnitude of the energy gap, and a plethora of different curves for the density of states [1].

The central difficulty is that tunneling is a surface probe, with information derived from a volume at the surface determined by the coherence length which can be as short as one unit cell [2]. A controlled experiment should therefore be accompanied by structural and chemical characterization of the surface. This in and of itself will not ensure a useful result, as the morphological and chemical complexity of the high-T_c materials, together with their sensitivity to disorder, can result in a surface very different from the bulk. The resultant data may not be representative of the bulk properties. Consequently, conclusions drawn from *all* tunneling measurements reported to date, including the present one, must be viewed with some caution. The emergence of photoemission [3,4] as an important probe of high-T_c superconductivity has been associated with the view that in such studies, surface conditions are largely under control.

A possible approach to transcending the difficulties of tunneling experiments would be to identify common features of data obtained from measurements subject to independent systematic errors, possibly involving the use of different tunneling geometries or the pursuit of entirely different types of measurement. Historically, the comparisons of electron-phonon spectral functions of conventional superconductors, as determined by tunneling, with phonon spectra determined by neutron scattering have been the most quantitative examples of this approach. Recently, such a comparison was carried out for $Ba_{1-x}K_xBiO_3$ and $Nd_{2-x}Ce_xCuO_{4-y}$ [5].

An alternative approach would be to obtain tunneling spectra by vacuum tunneling into a surface which is also clearly imaged, using the same tip, in the scanning-tunneling-microscope (STM) mode. In this Letter we report the results of such a study carried out on a high-quality $Bi_2Sr_2CaCu_2O_x$ single crystal. Current-voltage characteristics of a BCS-like nature with energy-gap values $\Delta \approx 30$ meV were found, in agreement with previous studies of this sort [6,7]. These spectroscopic measurements were obtained at positions near the center of the STM image, which itself was obtained at low temperatures. Most significantly, a second peak in the conductance at 90 meV, or around 3Δ, was observed. A feature of this sort has been predicted by the phenomenological Fermi-liquid model [8].

The low-temperature STM, which was of tubular design, was placed inside a vacuum can immersed in liquid helium. It was calibrated by scanning the surface of a single crystal of graphite at 4.2 K. The superconducting transition temperature T_c and the transition width (10%–90%) of the single crystal of $Bi_2Sr_2CaCu_2O_x$ were determined, magnetically, to be 85 K and less than 2 K, respectively. The tunneling structure was prepared in the following manner: The crystal was cleaved in air immediately before being positioned in the low-temperature apparatus. The STM tip was then placed over a highly faceted region on the cleaved surface such that direct tunneling into a combination of the *c* direction and the *a-b* plane would be possible. This was intended to facilitate some tunneling into the *a-b* plane, which would increase the chances of probing superconducting properties, as the coherence length is larger in that direction than in the *c* direction. In some studies the tip was positioned over a flat surface, thus confining the tunneling to the *c* direction.

The techniques used to obtain the STM images resolving atoms at low temperatures, as shown in Fig. 1, have been described in our earlier work [9]. Although substantial detail is evident in Fig. 1, and the overall pattern is in agreement with previous reports of atomic resolution

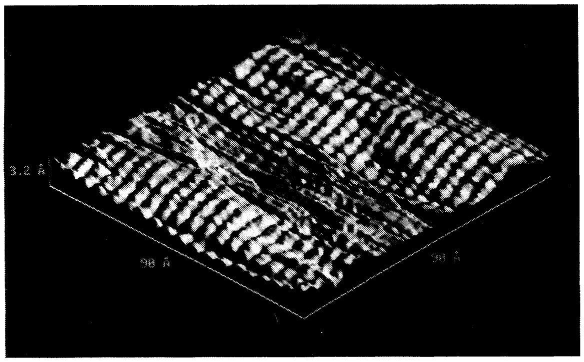

FIG. 1. Scanning-tunneling-microscope image of the *a-b* plane of a $Bi_2Sr_2CaCu_2O_x$ crystal taken at 6.4 K. The tip bias was +0.1 V and the tunneling current was 1 nA. The *a*-axis lattice parameter is estimated to be 5.0 Å.

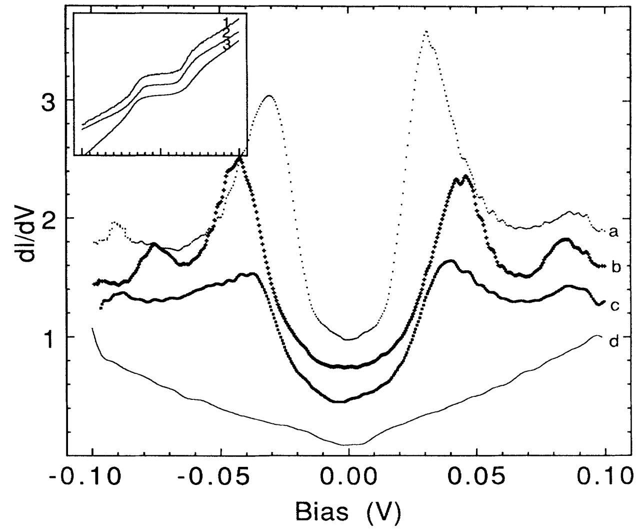

FIG. 2. Four representative plots of dI/dV-V characteristics normalized to unity at 100 mV and shifted vertically for clarity. The conductance peak resembling the BCS energy-gap feature is apparent in three curves (labeled *a*, *b*, and *c*) obtained at positions near the center of the faceted field imaged in Fig. 1. The features near ±90 meV are evident in these traces. Curve *d* was obtained from a region which was unfaceted, as determined by STM, and corresponds to the case of tunneling in the *c* direction. The inset displays three *I-V* characteristics with peak-to-peak tunneling currents of 20, 40, and 100 nA, respectively. These are normalized and shifted vertically for clarity. They differ in the tip-to-crystal distance. Curve *a* of the main part of the figure is the derivative of curve 2 of the inset.

in $Bi_2Sr_2CaCu_2O_x$ at room temperature [10] and at low temperatures [6,7,11], there was an instability which resulted in our not knowing the exact position of the tip during a specific measurement of an *I-V* characteristic. It is known to be near the center of Fig. 1. Several tens of characteristics, interleaved with determinations of the image, were obtained. The *I-V* characteristics were not stable indefinitely at nominally the same tip position, a reflection of the instability. It should be noted that it was not possible to fix the position of the tip while temperature was being changed.

Current-voltage characteristics were obtained with the feedback off over a 100-ms interval. The maximum bias voltage was 100 mV. The fact that by changing the vertical position of the STM tip it was possible to reversibly vary the tunneling current at fixed bias and fixed tip position over about two decades is evidence that the STM tip was not operating in a point-contact mode. The broadening of the characteristics as the vertical position of the tip was moved closer to the surface without touching it has previously been observed in our laboratory in STM studies of Pb films which exhibited an unequivocal superconducting gap. The effect is probably a consequence of an increase in pair breaking by the tunneling current itself, as the latter is increased. This suggests that these features are due to superconductivity, and are neither Coulombic effects nor a consequence of a semiconducting layer on the surface. When the point-contact mode was entered by producing a tip crash, the atomic resolution images disappeared and *I-V* characteristics of the type exemplified by representative curves *a*, *b*, and *c* of Fig. 2 were lost and replaced by a multiple-peak structure similar to that reported in Ref. [7].

The large peaks in the conductance of curves *a*, *b*, and *c* of Fig. 2 are identified, by analogy with low-T_c superconductors, as signatures of the energy gap. The conductance near zero bias in some traces is quite low relative to previously reported data on cuprate superconductors. The lowest zero-bias conductances correspond to a ratio of the normal-state conductance to the zero-bias conductance larger than 12, and in these instances density of states is approximately conserved. This would not be the case if leakage, semiconductor, or Coulomb blockade effects dominated the data. A further argument against Coulomb blockade effects is that no grains were imaged, as was the case in our previous work in which the blockade was directly associated with imaged grains [9]. In our attempts at tunneling into the *c* direction, for which the tip was positioned at an unfaceted part of the surface (curve *d* of Fig. 2), the widely reported linear dI/dV-V characteristics were found [12].

As is common to all published tunneling data on high-T_c superconductors, dI/dV-V characteristics were broadened an order of magnitude in excess of what would be expected from thermal processes (~0.5 meV at T=6.5 K). For *I-V* characteristics, which were the least broadened, existing models such as the BCS theory incorporating finite quasiparticle lifetime broadening or strong-coupling effects [1,13] could not be satisfactorily fitted to the data. However, for a few curves with less distinctive gap features, a fit could be made by replacing the excitation energy E by $E - i\Gamma$ in the density of states, thus treating Γ as the broadening parameter [13]. This led to values of Δ and Γ of the order of 32 and 7 meV, respectively, consistent with estimates in some previous studies [1,6,7,14].

The many I-V characteristics obtained in this work were different, certainly the result of the tip being positioned at locations with different atomic environments, and possibly a consequence of tunneling into different crystalline directions exhibiting different pair potentials [1,15]. Alternatively, there may be inclusions at a particular location of other Bi-Sr-Ca-Cu-O phases with different (higher) transition temperatures. A statistical distribution of the voltages at which the peak of the gap feature was found is plotted in Fig. 3(a). The spread is from 30 to 50 meV. Traces exhibiting the largest gaps were those which were most broadened. The best-defined peaks in the conductance were those with the lowest gaps ($\Delta \approx 30$ meV), leading to a ratio of $2\Delta/kT_c \approx 8.2$, approximately the value found in high-resolution photoemission measurements [3,4], and in several tunneling studies of $Bi_2Sr_2CaCu_2O_x$ [6,7,14].

The second peak was found in all of the dI/dV-V characteristics exhibiting a gap feature. Its position in voltage at a given lateral position of the tip was independent of the tip-to-crystal distance, which was also true of the main peak. Figure 3(b) shows a histogram of the voltages at which this peak was found, derived from 38 dI/dV-V curves. The distribution is centered around 90 ± 2 meV, a value 3 times that of the lowest energy-gap feature. Effects with possibly the same physical origin as the 90-meV feature have been observed in other studies. A dip (not a peak) has been seen in the density of states near 90 meV in a photoemission study [4], and a peak in the density of states at approximately 4Δ has been reported in a break-junction measurement [16]. The latter involves a superconductor-insulator-superconductor (SIS) tunneling configuration rather than a superconductor-insulator-normal (SIN) geometry. The observation of a 4Δ peak in a SIS configuration is consistent with a 3Δ peak in a SIN configuration, implying the presence of a common feature in the quasiparticle spectral densities. The fact that both of these other studies are presumably subject to systematic errors different from those of the present work, provides support for the idea that the peak at 3Δ is not an artifact. However, it should be noted that there was no sign of a 3Δ feature in either the work of Ref. [7], which was an investigation similar in nature to the present study, albeit with lower signal-to-noise ratio, or in optical experiments [17].

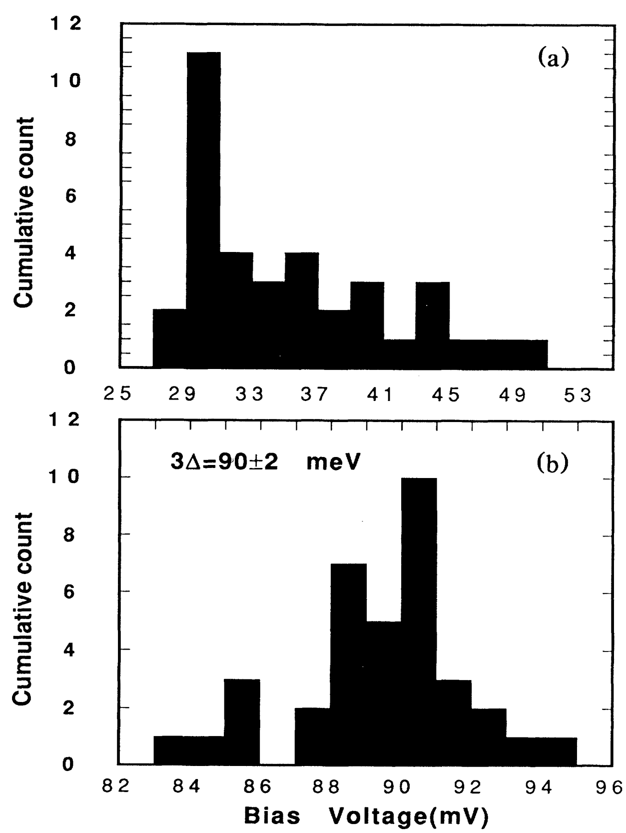

FIG. 3. (a) Histogram of the voltages of the feature associated with the energy gap. (b) Histogram of the voltages of the second feature in the tunneling characteristic. The peak in the distribution is at 90 ± 2 meV which is approximately 3 times the gap voltage.

It is significant that the histograms for the main and 90-meV peaks are not the same. The former disperse upward from 29 to 30 meV, whereas the latter is symmetric about 90 meV, and exhibits far less dispersion. The second peak most frequently occurs at voltages 3 times that of the *lowest* value observed for the main peak. The observation of atomic images implies that tunneling between the tip and the superconductor is directional. Because data have been acquired with the tip positioned in the vicinity of a highly faceted region of the surface, traces at slightly different positions should result in tunneling into states for which the lowest energy corresponds to nonvanishing wave vectors (k). The lowest values of the conductance peak would then correspond to tunneling in which the threshold corresponded to $k=0$ and the peak voltage in this instance would be a measure of the energy gap Δ. Tunneling in which the threshold corresponded to $k \neq 0$ would give rise to conductance peaks at energies greater than the smallest observed, and because of the random positions of the tip, the histogram of peak voltages would scatter upward from the minimum value, as is observed.

Dispersion with k would not be expected for a feature in the spectral density associated with a spatially localized excitation, such as that described in the marginal-Fermi-liquid phenomenology [18]. In this model, a bosonic spectrum of particle-hole pairs, which have a binding energy of twice the energy gap in the superconducting state, provides a scattering channel for quasiparticles, leading to the feature at 3Δ in the single-particle spectral function. Because these excitations are spatially localized, the energy of their signature in the conductance would be k-vector independent. Thus dI/dV-V traces corresponding to different k vectors and different values of the voltage of the main peak would have their high-voltage features at the same fixed voltage. If the 90-meV feature were a band-structure effect, or were associated with an elastic process, it would disperse with k the same way the main peak does, resulting in a similar histogram. It could conceivably be a signature of an inelastic process, but would have to involve a localized excitation. In this instance, it would be hard to see why it would occur at an energy 3 times that of the superconducting gap.

In summary, a STM study has been carried out on a $Bi_2Sr_2CaCu_2O_x$ crystal at low temperatures. The arrangement of the surface atoms was observed and the dI/dV vs B characteristics yield the ratio $2\Delta/k_BT_c \approx 8.2$, and reveal a peak in the density of states at 3Δ. The latter implies the existence of a localized excitation such as that suggested in the marginal-Fermi-liquid picture.

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[1] For a recent review, see J. R. Kirtley, Int. J. Mod. Phys. B **4**, 201 (1990).

[2] It should be noted that a short coherence length in and of itself may not be an impediment to obtaining useful results from tunneling. Model calculations based on the BCS theory suggest that the order parameter near the surface is not suppressed, as is implied by the de Gennes generalization of the Ginzburg-Landau boundary conditions. See T. Giamarchi, M. T. Béal-Monod, and Oriol T. Valls, Phys. Rev. B **41**, 11033 (1990).

[3] J-M. Imer, F. Patthey, B. Dardel, W. D. Schneidel, Y. Baer, Y. Petroff, and A. Zettl, Phys. Rev. Lett. **62**, 336 (1989); C. G. Olson, R. Liu, A-B. Yang, D. W. Lynch, A. J. Arko, R. S. List, B. W. Veal, Y. C. Chang, P. Z. Jiang, and A. P. Paulikas, Science **245**, 731 (1989).

[4] D. S. Dessau, B. O. Wells, Z-X. Shen, W. E. Spicer, A. J. Arko, R. Slist, D. B. Mitzi, and A. Kapitulnik, Phys. Rev. Lett. **66**, 2160 (1991).

[5] Q. Huang, J. F. Zasadzinski, N. Tralshawala, K. E. Gray, D. G. Hinks, J. L. Peng, and R. L. Greene, Nature (London) **347**, 369 (1990).

[6] Chen Wang, B. Giambattista, C. G. Slough, R. V. Coleman, and M. A. Subramanian, Phys. Rev. B **42**, 8890 (1990).

[7] Tetsuya Hasegawa, Masashi Nantoh, and Koichi Kitzazawa, Jpn. J. Appl. Phys. **30**, L276 (1991).

[8] C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. Ruckenstein, Phys. Rev. Lett. **63**, 1996 (1989); **64**, 497(E) (1990); P. B. Littlewood and C. M. Varma, AT&T Bell Laboratories report, 1991 (to be published).

[9] J-C. Wan, K. A. McGreer, K. M. Beauchamp, B. R. Johnson, J-X. Liu, T. Wang, and A. M. Goldman, Physica (Amsterdam) **165&166B**, 1505 (1990).

[10] C. K. Shih, R. M. Feenstra, J. R. Kirtley, and G. V. Chandrasekhar, Phys. Rev. B **40**, 2682 (1989).

[11] T. Hasegawa, M. Nantoh, H. Suzuki, N. Motohira, K. Kishio, and K. Kitazawa, Physica (Amsterdam) **165&166B**, 1563 (1990).

[12] M. Gurvitch, J. M. Valles, Jr., A. M. Cucolo, R. C. Dynes, J. P. Garno, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. Lett. **63**, 1008 (1989); J. Geerk, X. X. Xi, and G. Linker, Z. Phys. B **73**, 329 (1988).

[13] R. C. Dynes, J. P. Garno, G. B. Hertl, and T. P. Orlando, Phys. Rev. Lett. **53**, 2437 (1984); Zhao Shiping, Tao Hongjie, Chen Yinfei, Yan Yifen, and Yang Qianshen, Solid State Commun. **67**, 1179 (1988).

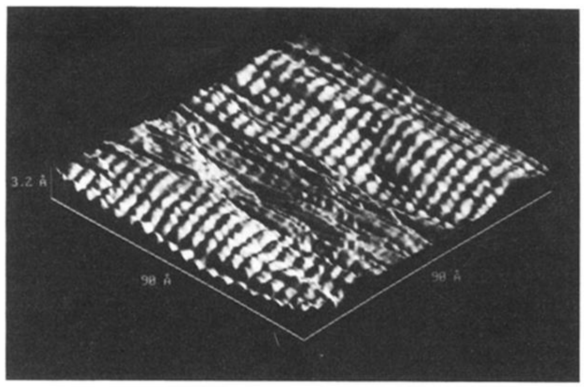
[14] Mark Lee, D. B. Mitzi, A. Kapitulnik, and M. R. Beasley, Phys. Rev. B **39**, 801 (1989); H. Ikuta, A. Maeda, K. Uchinokura, and S. Tanaka, Jpn. J. Appl. Phys. **27**, L1038 (1988); see also H. Maeda, Y. Tanaka, M. Fukutomi, and T. Axano, *ibid.* **27**, L6611 (1988).

[15] 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); J. S. Tsai, I. Takeuchi, J. Fujitu, T. Yushitake, S. Miura, S. Tanaka, T. Terashima, Y. Bando, K. Iijima, and K. Yamamoto, Physica (Amsterdam) **153-155C**, 1385 (1988).

[16] L. Forro, D. Mandrus, C. Kendziora, and L. Mihaly, Phys. Rev. Lett. (to be published).

[17] G. Thomas (private communication).

[18] P. Littlewood and C. M. Varma (private communication).



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