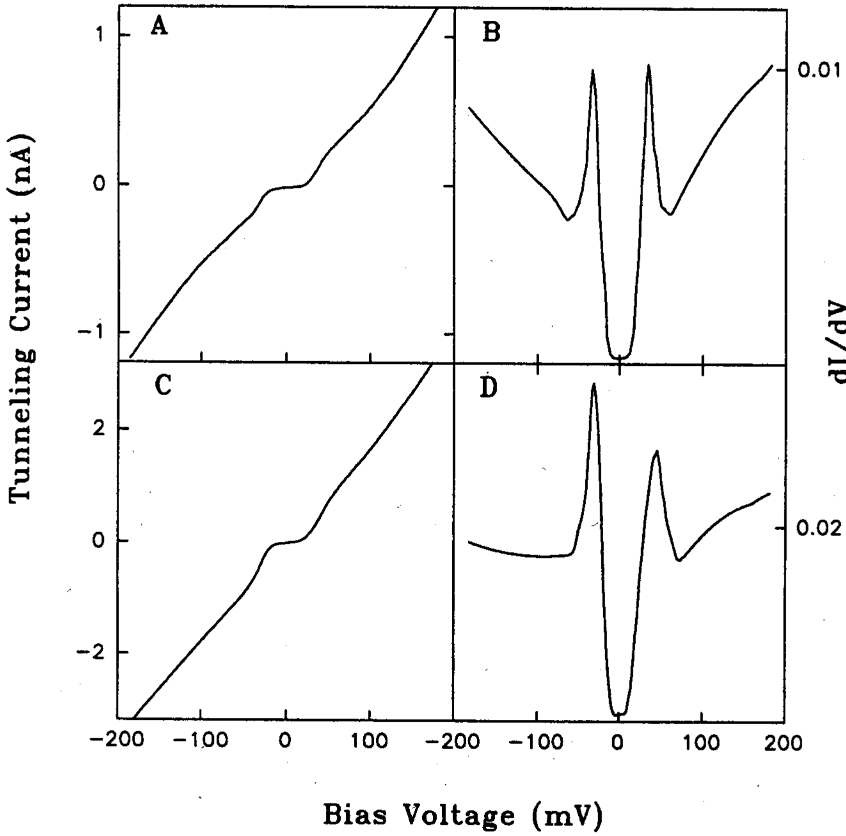

Figure 12. A and C: Typical I–V *curves obtained on oxygen-annealed $Bi_2Sr_2CaCu_2O_8$ single crystals at 4.2 K. These NIS junctions were formed between a Pt–Ir tip and cleaved $Bi_2Sr_2CaCu_2O_8$ crystal surfaces. B and D: Conductance (dI/dV) versus voltage curves corresponding to the* I–V *data in A and C, respectively. The curves exhibit well-developed gap structure and linear background conductance for* $|V| > \pm\Delta$. *Conductances at* V = *0 in B and D are 8 and 5%, respectively, of* G*(100).*

Qualitatively, the *I–V* curves exhibit a flat, low-current region about the Fermi level (E_f, $V = 0$) and relatively sharp conductance onsets at ±25 mV. These features are characteristic of a conventional superconducting energy gap. Interestingly, this well-developed gap structure is observed reproducibly over the surfaces of oxygen-annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples. In contrast, we observe a wide range of *I–V* behavior on as-grown $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples; these variations are similar to those found in other reports (*63*). Therefore, much of the uncertainty observed in previous work may be due to oxygen nonstoichiometry. In the following sec-

tion, we confine our analysis solely to reproducible measurements obtained on oxygen-annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples.

The conductance, $G(V) = dI/dV$, versus voltage curves provide essential insight into the nature of the superconducting gap in these materials (Figures 12C and 12D). The conductance within the gap is low. For the NIS junctions, $G(0)/G(150)$ values, where $G(150)$ is representative of the normal-state conductance, are between 2 and 8%. These values can be compared with conductances of 30–50% reported previously (*59, 62, 63*).

We do find, however, large conductances in tunneling measurements made on the as-grown $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals. Because extrinsic effects such as sample inhomogeneity were not accounted for in the previous tunneling studies, these previous data are not necessarily indicative of d-wave pairing or gapless superconductivity. In our carefully annealed samples, $G(V)$ is very low at $V = 0$; however, the behavior of $G(V)$ for $V > 0$ is also important to consider.

First, the increase in $G(V)$ within the gap is not proportional to $|V|$. A linear increase in $G(V)$ would be a clear signature for gapless superconductivity (*60*); therefore, our results may argue against this possibility. Comparing the conductance at $V = 0$ and $V = \Delta/2$ predicted for s-wave BCS gap with our data, we find that the increase in $G(V)$ at $V = \Delta/2$ is close to or slightly larger than the increase predicted by a thermally broadened (4.2 K) BCS-gap expression (*see* Figures 12C and 12D, respectively). These results indicate close analogy to a conventional BCS-like gap; however, the divergence at the gap edge differs from conventional behavior.

Similar results were also obtained from SIS junctions; representative I–V and $G(V)$ curves are shown in Figure 13. The I–V curves exhibit a flat, low-current region about $V = 0$ and pronounced conductance onsets at approximately ±50 mV. The near-zero current region about E_f detected in the SIS measurements is approximately 2 times larger than in the NIS data. This observation is consistent with the measurement of 2Δ and 4Δ in the NIS and SIS junctions, respectively, and indicates that other effects such as the Coulomb blockade do not contribute significantly to our data.

The $G(V)$ curves from the SIS junctions also exhibit low conductance at E_f (~4%). The background conductance within the gap increases more rapidly than does the background conductance found for the NIS junctions. The increase in conductance could be due to either poor junction quality or gapless superconductivity. Poor SIS junction quality is probably the major factor leading to the increase in $G(V)$ within the gap; however, we do not have sufficient experimental evidence at this time to resolve the observed differences in the gap excitations for the NIS and SIS junctions. Regardless of the origin of the excitations observed in the gap of these SIS junctions, these data confirm the magnitude of 2Δ for the oxygen-

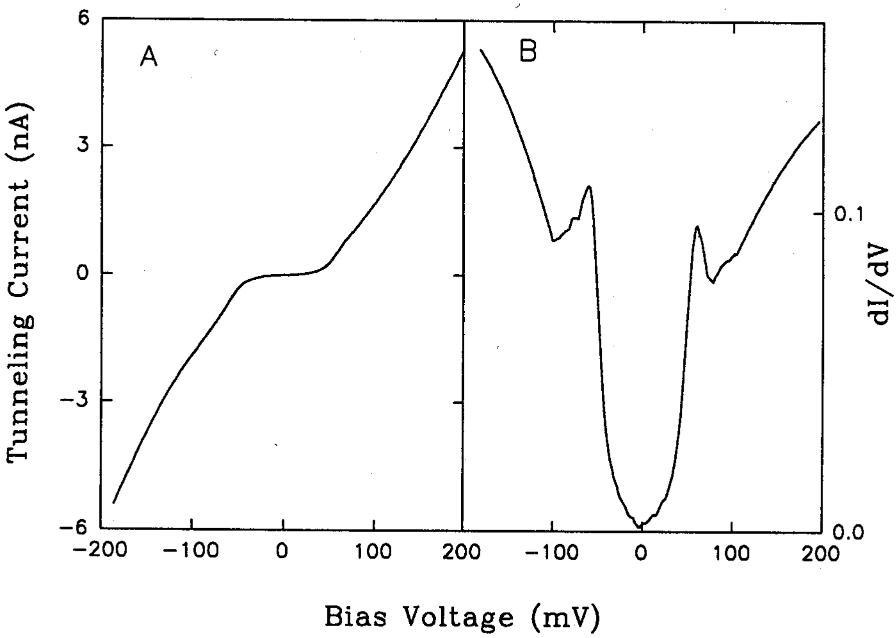

Figure 13. A: Representative I–V *curve obtained from an SIS junction formed between two oxygen-annealed* $Bi_2Sr_2CaCu_2O_8$ *crystals at 4.2 K. The junction geometry averages the* c *and* a–b *directions. B: Conductance versus voltage curve corresponding to the data in A. The conductance at* V = 0 *is 4% of* G(100). *The gap structure observed in the SIS junctions exhibits greater broadening than the data obtained from the NIS junction.*

annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals and provide a consistent and reproducible energy scale for superconductivity.

In addition, we further analyzed the reproducible gap structure observed in our NIS measurements to quantitatively assign a value to 2Δ and to probe the energy dependence of the DOS. The experimental data were fit to the following modified BCS model for DOS:

$$N_S = R_e\{(eV - i\Gamma)/[(eV - i\Gamma)^2 - \Delta^2]^{1/2}\} \qquad (12)$$

where Γ is a phenomenological parameter to account for broadening, N_S is the density of states in the superconducting state, R_e corresponds to the real part of the complex number in braces {}, and i is $\sqrt{-1}$.

A typical fit using this model is shown in Figure 14. The experimental data are well-fit for $|V| < \Delta/2$, but the experimental conductance peaks are broadened significantly compared with the model DOS. Similar

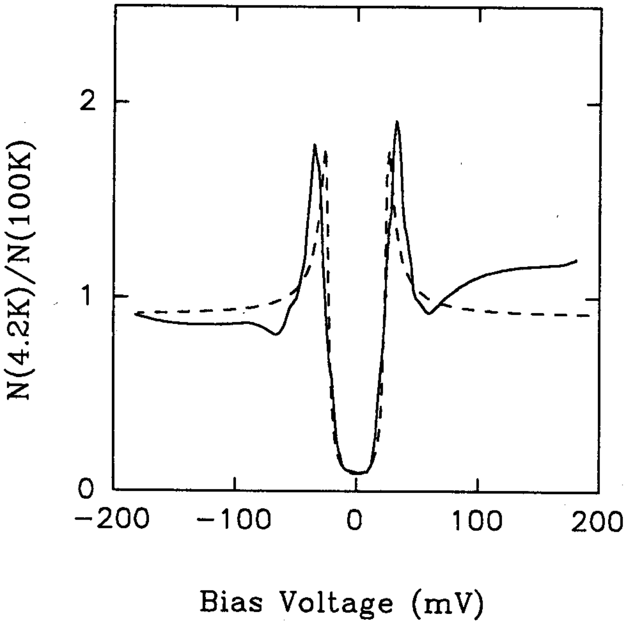

Figure 14. Conductance determined at 4.2 K normalized by the conductance at 100 K, G(4.2 K)/G(100 K), versus voltage for a typical NIS junction (solid line). The dashed line corresponds to a fit of this experimental data to the BCS model for DOS (see *equation 12). This simple model for the superconducting state fits the gap structure well, although the experimental conductance peaks are significantly broader than the model fit. The values of Δ and Γ extracted from the model fit are 25 and 3 meV, respectively.*

fits were also obtained for other $G(V)$ data with $\Gamma = 1$–3 meV; this broadening energy is greater than the thermal energy (0.36 meV). One should not, however, place too much significance on Γ because sample quality may still be limiting. That is, the finite transition widths indicate that the samples are not perfectly crystalline.

Nevertheless, this analysis has several different points. First, the well-defined gap in the NIS data can be fit at low energies by using a conventional model, although the broadening needed for a best-fit is greater than expected for only thermal effects. Second, the magnitudes of 2Δ and 4Δ extracted from our fits to the NIS and SIS data, 50 ± 5 and 98 ± 5 mV, respectively, show that the energy scale for superconductivity is ~$6.8kT_c$. The magnitude of 2Δ extracted from this analysis is, therefore, consistent with high-resolution, electron energy loss spectroscopic and photoemission spectroscopic measurements of $Bi_2Sr_2CaCu_2O_{8+\delta}$ crystals

(*66, 69, 70*). Lastly, the divergence in the experimental data at the gap edge is weak in comparison with the behavior expected for an s-wave BCS superconductor. This deviation from conventional behavior may be a signature of d-wave pairing or gapless superconductivity, although additional studies will be needed to confirm the intrinsic nature of the divergence.

These low-temperature STS studies of homogeneous, oxygen-annealed $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals have shown that a well-developed gap structure can be observed reproducibly in high-quality samples. The low conductance and change of $G(V)$ observed within the gap region differ from the behavior expected for either a gapless or BCS-like superconductor and may indicate d-wave pairing. Analyses of data from both NIS and SIS junctions provide a consistent scale for superconductivity with $2\Delta \approx 6.8kT_c$.

Summary and Conclusions

STM and STS were used to characterize the electronic and structural properties of the high-temperature copper oxide superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$. In particular, these studies have done the following:

1. elucidated the local structural order in the BiO layer of $Bi_2Sr_2CaCuO_8$ and the low-energy electronic states associated with this disorder
2. characterized the structural and electronic effects caused by reducing and increasing the oxygen concentration in this material
3. determined a consistent value for the magnitude of the superconducting energy gap in $Bi_2Sr_2CaCuO_{8+\delta}$ single crystals

These data represent a firm beginning of a detailed microscopic picture of the structural and electronic properties for these complex materials. Continued STM and STS studies will undoubtedly lead to a much clearer understanding of superconductivity in the copper oxides. We believe that the use of STM and STS will also provide essential insight into many other problems in materials chemistry.

Acknowledgments

Charles M. Lieber thanks David and Lucile Packard of the National Science Foundation, Camille and Henry Dreyfus Foundation, and the A. P. Sloan Foundation for generous support of this work.

References

1. Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. *Phys. Rev. Lett.* **1982,** *49,* 57.
2. Golovchenko, J. A. *Science (Washington, D.C.)* **1986,** *232,* 48.
3. Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Science (Washington, D.C.)* **1986,** *234,* 304.
4. Hamers, R. J. *Annu. Rev. Phys. Chem.* **1989,** *40,* 531.
5. Griffith, J. E.; Kochanski, G. P. *Annu. Rev. Mater. Sci.* **1990,** *20,* 194.
6. Avouris, P. *J. Phys. Chem.* **1990,** *94,* 2246.
7. Lieber, C. M.; Wu, X. L. *Acc. Chem. Res.* **1991,** *24,* 170.
8. Coleman, R. V.; Giambattista, B.; Hansma, P. K.; Johnson, A.; McNairy, W. W.; Slough, C. G. *Adv. Phys.* **1988,** *37,* 559.
9. Wu, X. L.; Lieber, C. M. *Science (Washington, D.C.)* **1989,** *243,* 1703.
10. Wu, X. L.; Lieber, C. M. *Phys. Rev. Lett.* **1990,** *64,* 1150.
11. Wu, X. L.; Lieber, C. M. *J. Am. Chem. Soc.* **1989,** *111,* 2731.
12. Chen, H.; Wu, X. L.; Lieber, C. M. *J. Am. Chem. Soc.* **1990,** *112,* 3326.
13. Wu, X. L.; Zhou, P.; Lieber, C. M. *Phys. Rev. Lett.* **1988,** *61,* 2604.
14. Wu, X. L.; Zhou, P.; Lieber, C. M. *Nature (London)* **1988,** *335,* 55.
15. Wu, X. L.; Lieber, C. M. *Phys. Rev. B.* **1990,** *41,* 1239.
16. Dai, H.; Chen, H.; Lieber, C. M. *Phys. Rev. Lett.* **1991,** *66,* 3183.
17. Wang, C.; Giambattista, B.; Slough, C. G.; Coleman, R. V. *Phys. Rev. B* **1990,** *42,* 8890.
18. Rao, C. N. R.; Raveau, B. *Acc. Chem. Res.* **1989,** *22,* 106.
19. Torardi, C. C.; Subramanian, M. A.; Calabrese, J. C.; Gopalakrishnan, J.; Morrissey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdhry, U.; Sleight, A. W. *Science (Washington, D.C.)* **1988,** *240,* 631.
20. Hansma, P. K.; Tersoff, J. *J. Appl. Phys.* **1987,** *61,* R1. Hansma, P. K.; Elings, V. B.; Marti, O.; Bracker, C. E. *Science (Washington, D.C.)* **1988,** *242,* 209.
21. Kuk, Y.; Silverman, P. J. *Rev. Sci. Instrum.* **1989,** *60,* 165.
22. Sakurai, T.; Hashizume, T.; Kamiya, I.; Hasegawa, Y.; Sano, N.; Pickering, H. W.; Sakai, A. *Prog. Surf. Sci.* **1990,** *33,* 3.
23. Tersoff, J.; Hamann, D. R. *Phys. Rev. Lett.* **1983,** *50,* 1998.
24. Tersoff, J.; Hamann, D. R. *Phys. Rev. B* **1985,** *31,* 805.
25. Lang, N. D. *Phys. Rev. Lett.* **1986,** *56,* 1164.
26. Selloni, A.; Carnevalli, P.; Tosatti, P. E.; Chen, C. D. *Phys. Rev. B* **1986,** *33,* 5770.
27. Tersoff, J. *Phys. Rev. B* **1990,** *41,* 1235.
28. Chen, C. J. *Phys. Rev Lett.* **1990,** *65,* 448.
29. Bardeen, J. *Phys. Rev. Lett.* **1963,** *6,* 57.
30. Simmons, J. *J. Appl. Phys.* **1963,** *34,* 1793.
31. Lang, N. D. *Phys. Rev. B* **1988,** *37,* 10395.
32. Feenstra, R. M.; Stroscio, J. A.; Fein, A. P. *Surf. Sci.* **1987,** *181,* 295.
33. Whangbo, M.-H.; Torardi, C. C. *Acc. Chem. Res.* **1991,** *24,* 127.
34. Sleight, A. W. *Science (Washington, D.C.)* **1988,** *242,* 1539.
35. Ramakrishnan, T. V.; Rao, C. N. R. *J. Phys. Chem.* **1989,** *93,* 4414.
36. Subramanian, M. A.; Torardi, C. C.; Calabrese, J. C.; Gopalakrishnan, J.; Morrissey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdhry, U.; Sleight, A. W. *Science (Washington, D.C.)* **1988,** *239,* 1015.

37. Gao, Y.; Lee, P.; Coppens, P.; Subramanian, M. A.; Sleight, A. W. *Science (Washington, D.C.)* **1988,** *241,* 954.
38. Zandbergen, H. W.; Groen, W. A.; Mijlhoff, F. C.; van Tendeloo, G.; Amelinckx, S. *Physica C (Amsterdam)* **1988,** *156,* 325.
39. Bordet, P.; Capponi, J. J.; Chaillout, C.; Chenavas, J.; Hewat, A. W.; Hewat, E. A.; Hodeau, J. L.; Marezio, M. *Stud. High Temp. Supercond.* **1989,** *2,* 171.
40. Eibl, O. *Physica C (Amsterdam)* **1991,** *175,* 419.
41. Kirk, M. D.; Nogami, J.; Baski, A. A.; Mitzi, D. B.; Kapitulnik, A.; Geballe, T. H.; Quate, C. F. *Science (Washington, D.C.)* **1988,** *242,* 1673.
42. Wu, X. L.; Zhang, Z.; Wang, Y. L.; Lieber, C. M. *Science (Washington, D.C.)* **1990,** *248,* 1211.
43. Tanaka, M.; Takahashi, T.; Katayama-Yoshida, H.; Yamazaki, S.; Fujinami, M.; Okabe, Y.; Mizutani, W.; Ono, M.; Kajimura, K. *Nature (London)* **1989,** *339,* 691.
44. Zhang, Z.; Wang, Y. L.; Wu, X. L.; Huang, J. L.; Lieber, C. M. *Phys. Rev. B* **1990,** *42,* 1082.
45. Shih, C. K.; Feenstra, R. M.; Chandrashekhar, G. V. *Phys. Rev. B* **1991,** *43,* 7913. Shih, C. K.; Feenstra, R. M.; Kirtley, J. R.; Chandrashekhar, G. V. *Phys. Rev. B* **1989,** *40,* 2682.
46. Massidda, S.; Yu, J.; Freeman, A. J.; Krakauer, H.; Pickett, W. E. *Phys. Rev. Lett.* **1988,** *60,* 1665.
47. Torardi, C. C.; Jung, D.; Kang, D. B.; Ren, J.; Whangbo, M.-H. *Mater. Res. Soc. Symp. Proc.* **1989,** *156,* 295.
48. Cava, R. J. *Science (Washington, D.C.)* **1990,** *247,* 656.
49. Daeumling, M.; Seuntjens, J. M.; Larbalestier, D. C. *Nature (London)* **1990,** *346,* 332.
50. Jorgensen, J. D.; Pei, S.; Lightfoot, P.; Shi, H.; Paulikas, A. P.; Veal, B. W. *Physica C (Amsterdam)* **1990,** *167,* 571.
51. Wu, X. L.; Wang, Y. L.; Zhang, Z; Lieber, C. M. *Phys. Rev. B* **1991,** *43,* 8729.
52. Zhang, Z.; Lieber, C. M. *Phys. Rev. B* **1992,** *46,* 5845.
53. Shen, Z.-X.; Dessau, D. S.; Wells, B. O.; Olson, C. G.; Mitzi, D. B.; Lombardo, L.; List, R. S.; Arko, A. J. *Phys. Rev. B* **1991,** *44,* 12098.
54. Zhang, Z.; Chen, C. C.; Lieber, C. M.; Morosin, B.; Venturini, E. L.; Ginley, D. S. *Phys. Rev. B* **1992,** *45,* 987.
55. Bardeen, J.; Cooper, L. N.; Schrieffer, J. R. *Phys. Rev.* **1957,** *108,* 1175.
56. Giaever, I. *Phys. Rev. Lett.* **1960,** *5,* 147.
57. Kirtley, J. R. *Int. J. Mod. Phys. B* **1990,** *4,* 201.
58. Hasegawa, T.; Ikuta, H.; Kitazawa, K. In *Physical Properties of High Temperature Superconductors III;* Ginsberg, D. M., Ed.; World Scientific Publishing: River Edge, NJ, 1992; p 525.
59. Valles, J. M.; Dynes, R. C.; Cucolo, A. M.; Gurvitch, M.; Schneemeyer, L. F.; Garno, J. P.; Waszczak, J. V. *Phys. Rev. B* **1991,** *44,* 11986.
60. Mandrus, D.; Forro, L.; Koller, D.; Mihaly, L. *Nature (London)* **1991,** *351,* 460.
61. Boekholt, M.; Hoffmann, M.; Guntherodt, G. *Physica C (Amsterdam)* **1991,** *175,* 127.

62. Huang, Q.; Zasadzinski, J. F.; Gray, K. E.; Liu, J. Z.; Claus, H. *Phys. Rev. B* **1989,** *40,* 9366.
63. Liu, J.-X.; Wan, J.-C.; Goldman, A. M.; Chang, Y. C.; Jiang, P. Z. *Phys. Rev. Lett.* **1991,** *67,* 2195.
64. Tao, H. J.; Chang, A.; Lu, F.; Wolf, E. L. *Phys. Rev. B* **1992,** *45,* 10622.
65. Chen Q.; Ng, K.-W. *Phys. Rev. B* **1992,** *45,* 2569.
66. Li, Y.; Huang, J. L.; Lieber, C. M. *Phys. Rev. Lett.* **1992,** *68,* 3240.
67. Zhang, Z.; Lieber, C. *Phys. Rev. B* **1993,** *47,* 3423.
68. Wolf, E. L. *Principles of Tunneling Spectroscopy;* Oxford University Press: New York, 1989.
69. Olson, C. G.; Liu, R.; Yang, A.-B.; Lynch, D. W.; Arko, A. J.; List, R. S.; Veal, B. W.; Chang, Y. C.; Jiang, P. Z.; Paulikas, A. P. *Science (Washington, D.C.)* **1989,** *245,* 731.
70. Dessau, D. S.; Wells, B. O.; Shen, Z.-X.; Spicer, W. E.; Arko, A. J.; List, R. S.; Mitzi, D. B.; Kapitulnik, A. *Phys. Rev. Lett.* **1991,** *66,* 2160.

RECEIVED for review November 9, 1992. ACCEPTED revised manuscript April 8, 1993.

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Leonard V. Interrante, Lawrence A. Casper and Author B. Ellis, Editors