Intrinsic features of $Bi_2Sr_2CaCu_2O_{8+\delta}$ tunneling spectra: Scaling and symmetry of the energy gap

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Tunneling measurements have been made on a series of high-quality $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) single crystals with transition temperatures (T_c) ranging from 79 to 92 K. From these systematic studies it has been possible to delineate the intrinsic features of the low-energy electronic spectrum in the BSCCO materials. These results demonstrate that the magnitude of 2Δ at 4.2 K is nearly constant in the different T_c samples, and thus, that $2\Delta/kT_c$ increases as T_c decreases. In addition, intrinsic quasiparticle excitations are detected within the gap irrespective of the sample T_c's. Analyses of these electronic spectra using a variety of pairing models suggest that gap functions having a large anisotropy can provide a good fit to the experimental data.

The mechanism of superconductivity in the high-temperature copper oxide superconductors is an unresolved and challenging problem.[1-6] The energy gap (2Δ) is one parameter of the superconducting state that can provide significant insight into the mechanism of pairing. For example, the magnitude, temperature dependence, and symmetry of 2Δ are strong constraints for models proposed to explain superconductivity in the copper oxide materials. In principle, these properties of 2Δ should be readily determined using established experimental probes such as tunneling and photoemission spectroscopy (PES). Unfortunately, the surface sensitivity of these techniques coupled with short coherence lengths and inhomogeneity of the copper oxide materials has often made these measurements difficult to interpret clearly.

Nevertheless, there is now a reasonable consensus that the magnitude of 2Δ exceeds significantly the weak-coupling limit of $3.5kT_c$ and that the energy gap opens sharply below T_c.[7-12] Other important characteristics of 2Δ, which are essential to understanding the pairing mechanism, remain controversial. For example, high-resolution electron-energy-loss spectroscopy (HREELS) studies indicate that $2\Delta/kT_c$ increases as sample T_c decreases,[13] while other tunneling[14] and PES (Ref. 15) studies suggest that this ratio is constant. In addition, the nature of quasiparticle excitations within the gap (e.g., extrinsic or reflecting nodes in the gap function) and the symmetry of Δ have not been resolved.

Essential to understanding these issues is a clear delineation of the intrinsic versus extrinsic properties of the copper oxide materials. To this end we report systematic tunneling measurements on a series of high-quality $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) single crystals with transition temperatures (T_c) ranging from 79 to 92 K. Analysis of these data provides a clear indication of the intrinsic features of the low-energy electronic spectrum in the superconducting state of the BSCCO materials. Specifically, we find that the magnitude of 2Δ at 4.2 K is nearly constant in the different T_c samples and thus that $2\Delta/kT_c$ increases as T_c decreases. In addition, intrinsic quasiparticle excitations are observed within the gap irrespective of sample T_c. Comparison of these electronic spectra to a variety of pairing models shows that gap functions with large anisotropy provide a good fit to the experimental data.

BSCCO single crystals were grown in high-purity MgO oxide crucibles as described previously.[13] All of the crystals were extensively annealed to reduce strain and defects. Variations in the sample T_c were achieved by annealing crystals in 0.2–50 atm oxygen at temperatures $<550\,^{\circ}C$. These annealing conditions lead to reproducible variations in T_c without the formation of impurity phases. The homogeneity of these samples is clearly evident from the sharp transitions observed in dc-magnetization and resistivity measurements.[13] Representative magnetization data recorded on samples with T_c's of 79, 86, and 92 K are shown in Fig. 1. The uniformly

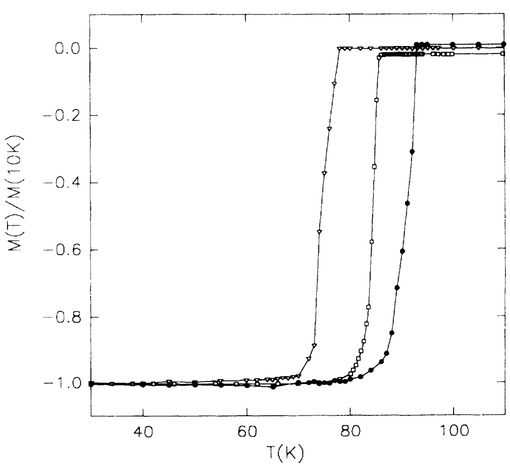

FIG. 1. Magnetization data recorded on $T_c=92$ K (●), 86 K (□), and 79 K (▽) BSCCO single crystals. The susceptibility measurements were recorded by cooling the samples in a field of 10 Oe.

narrow transition widths (≈ 2 K) observed for these annealed crystals are indicative of very homogeneous samples. Hence systematic tunneling studies of this series of materials represent a good approach by which to elucidate the intrinsic quasiparticle spectrum in BSCCO.

Tunneling measurements were made with a low-temperature scanning tunneling microscope (STM) using methods that have been detailed in a previous report.[11] Briefly, normal-metal–insulator–superconductor (NIS) junctions were formed between a sharpened Pt-Ir tip and freshly cleaved BSCCO crystals. Current (I) versus voltage (V) data were acquired digitally and numerically differentiated to obtain the conductance $[G(V)=dI/dV]$ curves. In these studies we have carried out tunneling measurements on at least three independent crystals at each of the three T_c's (i.e., 79, 86, and 92 K), and for each specific sample several I-V curves were recorded at more than 20 different locations.

Representative I-V curves recorded on three specific BSCCO crystals with T_c's of 79, 85, and 92 K are shown as insets in Fig. 2. The junction resistances in these experiments were varied between 10^6 and 10^8 Ω. For these conditions tunneling samples primarily the quasiparticle spectrum in the a-b plane.[16,17] The I-V curves recorded on $T_c=79$, 86, and 92 K BSCCO crystals all exhibit similar features including a relatively flat low-current region about $V=0$ and pronounced conductance onsets at $\pm(20-25)$ mV. These features agree qualitatively with expectations for a superconducting gap. The NIS character of several of the junctions was verified by temperature-dependent I-V measurements. Specifically, as the temperature approached and then exceeded the bulk sample, T_c the gap structure broadened and then disappeared.

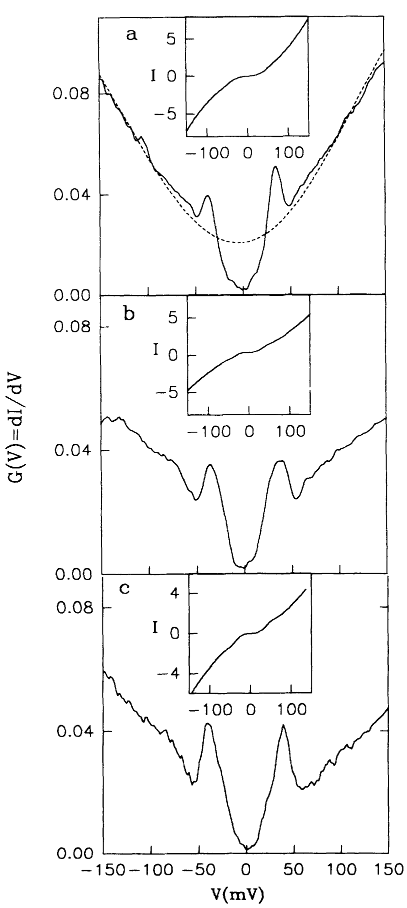

FIG. 2. Conductance $G(V)$ vs voltage data from $T_c=92$ K (a), 86 K (b), and 79 K (c) BSCCO single crystals. The dashed curve in (a) corresponds to the extrapolated normal-state conductance. The insets show the corresponding I-V data from which the $G(V)$ vs V curves were determined.

Clear insight into the electronic spectrum of the BSCCO samples in the superconducting state can be obtained from $G(V)$ since it is proportional to the density of states, N_s. The $G(V)$ vs V curves obtained on the samples with T_c's varying from 79 to 92 K all show similar features (Fig. 2). First, the conductance at zero bias, $G(V=0)$, is typically less than 5% of the normal-state conductance. The observation of reproducibly low conductances in all of these samples further indicates that $G(V)$ does reflect the quasiparticle spectrum and is not dominated by extrinsic effects since these would lead to large conductances at $V=0$. For example, chemical inhomogeneity could suppress T_c through improper doping. Inclusion of magnetic impurities could (through a pair-breaking effect) cause the superconducting state to be gapless. Both of these effects would lead to large conductances at $V=0$. The absence of a large conductance at $V=0$ also suggests that the barriers in our NIS junctions are good.[18,19] We thus believe that the reproducible features observed in our conductance data represent intrinsic features of the superconducting state in BSCCO and do not arise from extrinsic effects. These reproducible features include (1) excitations within the gap region for $|V|>0$, (2) well-defined conductance peaks, and (3) a linearly increasing background conductance. Below we focus on two important issues; these are (1) the dependence of 2Δ on sample T_c and (2) the nature of the quasiparticle excitations within the gap.

The magnitude of 2Δ can in principle be determined from conductance data since $G(V)\propto N_s$.[18] Such an analysis presupposes that the functional form of Δ and the relationship between N_s and Δ are known. However, without knowing the mechanism of high-T_c superconductivity, the correct functional forms of Δ and N_s remain an open question (see below). Hence the magnitude of 2Δ, as in previous studies,[11,12,14,20] must be assigned in a less rigorous manner. Here we determine 2Δ from (1) the intersection between the extrapolated background conductance and the gap structure, (2) a fit of $G(V)$ to models for the density of states, and (3) the peaks in $dG(V)/dV$.[21] Analyses carried out using these independent methods yield similar values for the magnitude of 2Δ.[21] There may be systematic errors in the magnitude of 2Δ determined by any of these methods; however, this error will be similar in the different T_c samples, and thus we believe that the trend in 2Δ vs T_c reported in this study is robust.

A summary of the values of 2Δ determined from a number of independent experiments on 79, 86, and 92 K T_c BSCCO samples is made in Table I. For these high-

TABLE I. Summary of results for the energy gap and reduced energy obtained on different T_c samples.

T_c (K)	2Δ (meV)	$2\Delta/kT_c$
91.8	52±2	6.6±0.2
85.5	50±2	6.8±0.2
79.0	50±3	7.4±0.4

quality samples, it is important to note that T_c at the sample surface, which was determined independently in temperature-dependent high-resolution electron-energy-loss spectroscopy studies,[10,13] are the same (±1 K) as the bulk T_c's determined by magnetization measurements. Hence our gap measurements can be correlated with the variations in sample T_c. These results show that within experimental error ($\pm 1\sigma$) the magnitude of 2Δ is constant in high-quality samples with T_c's varying nearly 15 K. Hence the reduced gap $2\Delta/kT_c$ increases with decreasing sample T_c (Table I). The increase in $2\Delta/kT_c$ with decreasing T_c is weak; however, a fit of this data to a constant for $2\Delta/kT_c$ does not lay within the experimental error bars. These results are in good agreement with our recent HREELS studies of BSCCO samples,[13] although they contrast the conclusions drawn from a previous tunneling study.[14] In the present study, measurements of 2Δ were made over a wider range of sample T_c's than in earlier tunneling studies and thus show a much clearer trend in $2\Delta/kT_c$ vs T_c. In addition, particular care was made to make measurements on homogeneous samples since crystal defects and nonstoichiometry have been shown to cause unpredictable variations in 2Δ (Ref. 11) and may also cause local variations in T_c. Hence we believe that the trends shown here represent the intrinsic behavior of the BSCCO superconductors.

As discussed previously, the increase in $2\Delta/kT_c$ as T_c decreases is suggestive of pair breaking.[13] Within this scenario the value of T_c is suppressed by increases in inelastic scattering as the samples are doped. If 2Δ, which sets the energy for interactions between pairs, is not affected by scattering, then $2\Delta/kT_c$ will increase as T_c is decreased. This is simply the standard model of pair breaking by magnetic impurities.[22,23] It is unlikely, however, that oxygen doping reduces T_c in this way.[13] An explanation more relevant to the copper oxide materials has been given by Monthoux, Balatsky, and Pines,[3,4] who suggest that T_c is reduced by quasiparticle scattering from spin fluctuations. Since the spin fluctuation correlation length (and hence scattering strength) depends on oxygen doping, this model might explain our data.[24] Although additional work will be needed to elucidate the origin of these results, the finding that 2Δ is essentially constant over a wide range of T_c's in BSCCO samples represents an important intrinsic property of these materials.

Last, we have also examined in detail the quasiparticle excitations within the gap region since these excitations provide insight into the symmetry of the gap function. We have found that $G(V=0)$ is consistently small (approaches zero), but for finite energies $G(V)$ increases rapidly and has sharp conductance peaks (Fig. 2). As discussed above, the reproducibility of these features in the different T_c samples suggests that they represent intrinsic behavior of the BSCCO system. There are several models from which it is possible to obtain significant electronic states within the gap region, including (1) broadened BCS s wave, (2) gapless, and (3) d wave. We assess the viability of the gap functions associated with these models by fitting to the normalized conductance data, N_s/N_n (Fig. 3).

One of the most common approaches used to fit $G(V)$ has been with a broadened BCS function.[11,12,20] An example of fits using the density-of-states function proposed

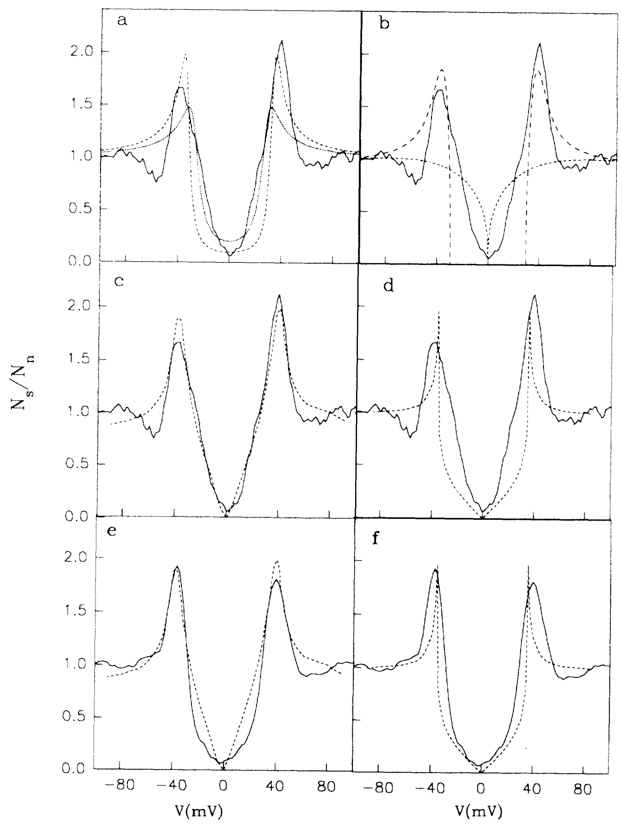

FIG. 3. Fits to a typical normalized conductance, N_s/N_n, vs voltage curve. In all cases the solid curve corresponds to the experimental data and the dashed lines to the fits. (a) Fits using a broadened BCS function $N_s/N_n = \mathrm{Re}\{(eV-i\Gamma)/[(eV-i\Gamma)^2-\Delta^2]^{1/2}\}$. The long-dashed line, which fits the conductance peaks but not the quasiparticle excitations within the gap, was made with $\Delta=32$ and $\Gamma=3.2$ meV. The short-dashed line, which provides a better fit to the excitations within the gap, was made with $\Delta=28$ and $\Gamma=5.7$ meV. (b) Fits using the standard pair-breaking model (Refs. 22 and 23). The long-dashed curve was fit using a small amount of pair breaking ($\alpha=\Gamma/\Delta=0.05$), while the short-dashed curve corresponds to the behavior expected for a gapless superconductor ($\alpha=1$). (c) The fit corresponds to N_s/N_n expected for a pure d-wave symmetry gap function; taken from Ref. 27. (d) A fit using the specific d-wave pairing model of Monthoux, Balatsky, and Pines (Ref. 3). (e), (f) Fits to the most rounded spectra (Ref. 29) using the pure d-wave and Monthoux-Balatsky-Pines models, respectively.

by Dynes, Narayanamura, and Garno[25] is shown in Fig. 3(a). This model does not provide a good fit to the experimental data since it cannot simultaneously have sharp conductance peaks and significant excitations within the gap. Hence we do not believe that this approach provides new insight into the physics of pairing. Alternatively, strong pair breaking can lead to quasiparticle excitations within the gap. This idea is further motivated by the observation that $2\Delta/kT_c$ increases as T_c is decreased (see above). For *s*-wave symmetry pairing, previous theoretical studies have shown that as inelastic scattering is increased the conductance peaks broaden and the observed gap (ω_g) gets smaller, but until the "gapless" regime is reached no quasiparticle excitations should be observed within the gap [Fig. 3(b)].[22,23] On the basis of previous tunneling studies, it has been suggested that BSCCO is gapless.[20] In the context of *s*-wave pairing, this description is inconsistent with the observation of sharp conductance peaks in previous studies and our present work [Fig. 3(b)]. Hence we believe that this model is too simple to describe adequately the high-T_c materials.

The fact that $G(V)$ is strongly peaked around $\pm\Delta$ and decreases gradually to a minimum at $V=0$ strongly suggests that there are nodes in the gap function. A function with *d*-wave symmetry (i.e., $d_{x^2-y^2}$: $\Delta(k)\sim\cos k_x a - \cos k_y a$) is one that will have nodes and also has the symmetry necessary to achieve pairing in several theoretical models.[2,3,6] Recent experimental studies have provided evidence for *d*-wave symmetry, although this critical point remains controversial.[26] We have carefully analyzed our data in terms of the energy dependent density of states predicted for a pure *d*-wave symmetry gap function[27,28] and for the specific *d*-wave symmetry gap model of Monthoux, Balatsky, and Pines[3] [Figs. 3(c)–3(f)]. The most typical experimental data [solid curves in Figs. 3(c) and 3(d)] are best fit by the pure *d*-wave gap function. The fit by the model of Monthoux, Balatsky, and Pines is worse, but still better than that observed for the *s*-wave models above. To examine the uncertainty in this analysis we have also analyzed a $G(V)$ spectrum that looks most like a conventional gap [Figs. 3(e) and 3(f)].[29] In this case the fit to the pure *d*-wave gap function is worse than for the Monthoux-Balatsky-Pines model; however, these models still fit this worst case data better than the above *s*-wave models. It is important to recognize, however, that a highly anisotropic *s*-wave gap function would exhibit many of the same features in tunneling spectra.[27,30] Hence we conclude that the tunneling data strongly support the idea of an anisotropic gap function, but do not distinguish conclusively between *d*-wave and anisotropic *s*-wave models. Measurements of the phase of the gap function will be needed to conclusively resolve this point.

In conclusion, systematic tunneling measurements of the electronic spectrum of high-quality BSCCO single crystals with T_c's ranging from 79 to 92 K have been made. From these studies it has been possible to delineate intrinsic features of the quasiparticle spectrum in BSCCO materials. Specifically, we find that the magnitude of 2Δ at 4.2 K is nearly constant in the crystals with T_c's varying nearly 15 K. Hence, in these oxygen-doped BSCCO crystals, the reduced energy gap $2\Delta/kT_c$ is not constant, but increases as T_c decreases. In addition, we find that there are intrinsic quasiparticle excitations within the gap irrespective of the T_c's of the BSCCO single crystals. Analyses of these data using a variety of pairing models suggest that highly anisotropic gap functions provide a good fit to the experimental data. To unambiguously determine the symmetry of the gap function (e.g., is it *s* or *d* wave) will, however, also require knowledge of its phase.

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[1] P. W. Anderson, Science **235**, 1196 (1987).

[2] J. R. Schrieffer, X.-G. Wen, and S.-C. Zhang, Phys. Rev. Lett. **60**, 944 (1988).

[3] P. Monthoux, A. V. Balatsky, and D. Pines, Phys. Rev. Lett. **67**, 3448 (1991); Phys. Rev. B **46**, 14 803 (1992).

[4] P. Monthoux and D. Pines, Phys. Rev. Lett. **69**, 961 (1992).

[5] C. M. Varma, P. B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A. E. Ruckenstein, Phys. Rev. Lett. **63**, 1996 (1989).

[6] A. Moreo, D. J. Scalapino, and S. R. White, Phys. Rev. B **45**, 7544 (1992).

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

[8] Y. Hwu, L. Lozzi, M. Marsi, S. La Rosa, M. Winokur, P. Davis, M. Onellion, H. Berger, F. Gozzo, F. Levy, and G. Margaritondo, Phys. Rev. Lett. **67**, 2573 (1991).

[9] J. E. Demuth, B. N. J. Persson, F. Holtzberg, and C. V. Chandrasekhar, Phys. Rev. Lett. **64**, 603 (1990); B. N. J. Persson and J. E. Demuth, Phys. Rev. B **42**, 8057 (1990).

[10] Y. Li, J. L. Huang, and C. M. Lieber, Phys. Rev. Lett. **68**, 3240 (1992).

[11] Z. Zhang and C. M. Lieber, Phys. Rev. B **47**, 3423 (1993).

[12] H. J. Tao, A. Chang, F. Lu, and E. L. Wolf, Phys. Rev. B **45**, 10 622 (1992); A. Chang, Z. Y. Rong, Y. M. Ivanchenko, F. Lu, and E. L. Wolf, *ibid.* **46**, 5692 (1992).

[13] Y. Li, J. Liu, and C. M. Lieber, Phys. Rev. Lett. **70**, 3494 (1993).

[14] L. Buschmann, M. Boekholt, and G. Guntherodt, Physica C **203**, 68 (1992).

[15] C. T. Simmons, S. L. Molodtsov, S. I. Fedoseenko, J. C. Allman, C. Laubschat, G. Kaindl, S. V. Moshikin, M. A. Kuzmina, M. U. Vlasov, and O. F. Vyvenko, Z. Phys. B **87**, 271 (1992).

[16] For the present weak contact junctions used in this study, the tunneling current can be written as $I \propto |\Psi(0)|^2 \exp(-2\kappa d)$, where d is the junction thickness and $\kappa=(2m\phi/\hbar^2+k_\parallel^2)^{1/2}$. Since there are no states at the Γ point, we observe tunneling with significant parallel momentum $k_\parallel$ (i.e., tunneling probes

states in the a-b plane).

[17]E. L. Wolf (unpublished).

[18]E. L. Wolf, *Principles of Tunneling Spectroscopy* (Oxford University Press, New York, 1989).

[19]G. E. Blonder, M. Tinkham, and T. M. Klapwijk, Phys. Rev. B **25**, 4515 (1982).

[20]Q. Huang, J. F. Zasadzinski, K. E. Gray, J. Z. Liu, and H. Claus, Phys. Rev. B **40**, 9366 (1989); J.-X. Liu, J.-C. Wan, A. M. Goldman, Y. C. Chang, and P. Z. Jiang, Phys. Rev. Lett. **67**, 2195 (1991).

[21]The intersection corresponds approximately to the midpoint of the gaplike structure. We have also determined the magnitude of 2Δ from fits using a broadened BCS density of states (Ref. 11), from the peaks in the derivative of the conductance data, $dG(V)/dV=(d^2I/dV^2)$, and from fits to the d-wave gap function. The values of 2Δ determined by these different methods are similar.

[22]A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1961) [Sov. Phys. JETP **12**, 1243 (1961)].

[23]K. Maki, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), p. 1035.

[24]A problem with this explanation for the BSCCO samples is that T_c is reduced by overdoping the crystals. Overdoping the materials should reduce the spin fluctuation correlation length, although an increase is needed to explain our data.

[25]R. C. Dynes, V. Narayanamura, and J. P. Garno, Phys. Rev. Lett. **41**, 1509 (1978).

[26]Z.-X. Shen, D. S. Dessau, B. O. Wells, D. M. King, W. E. Spicer, A. J. Arko, D. Marshall, L. W. Lombardo, A. Kapitulnik, P. Dickinson, S. Doniach, J. DiCarlo, A. G. Loeser, and C. H. Park, Phys. Rev. Lett. **70**, 1553 (1993).

[27]P. H. Dickinson and S. Doniach, Phys. Rev. B **47**, 11 447 (1993).

[28]C. Jiang, J. P. Carbotte, and R. C. Dynes, Phys. Rev. B **47**, 5325 (1993).

[29]Experimental data such as that shown in Figs. 3(e) and 3(f) was observed infrequently (5–10% of the time) compared with the typical data shown in Figs. 3(c) and 3(d).

[30]S. Chakravarty, A Sudbo, P. Anderson, and S. Strong, Science **261**, 337 (1993).