Giant Proximity Effect in Cuprate Superconductors

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Using an advanced molecular beam epitaxy system, we have reproducibly synthesized atomically smooth films of high-temperature superconductors and uniform trilayer junctions with virtually perfect interfaces. We found that supercurrent runs through very thick barriers. We can rule out pinholes and microshorts; this "giant proximity effect" (GPE) is intrinsic. It defies the conventional explanation; it might originate in resonant tunneling through pair states in an almost-superconducting barrier. GPE may also be significant for superconducting electronics, since thick barriers are easier to fabricate.

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Cuprate superconductors brought in several surprises. Above the critical temperature (T_c), they do not behave as conventional metals. Since high-temperature superconductor (HTS) state occurs so rarely in nature, one would indeed expect the superconducting state to be unusual as well—and yet so far it seemed rather conventional in most respects. A possible exception that has attracted theorist's attention recently [1–3] is the "giant proximity effect" (GPE). Indeed, several groups reported [4–11] that in Josephson junctions with HTS electrodes supercurrent can run through barriers as thick as 1000–10 000 Å, but such claims have been met with reservation because of conflict with the standard theoretical picture [12–14] and because of conceivable experimental problems, and the controversy about the experimental status of GPE has been ongoing for over a decade.

The standard theory was put forward by De Gennes [12] not long after Meissner discovered that a superconductor (S) and a normal metal (N) in close contact affect one another [15]. De Gennes attributed this proximity effect to Cooper pairs that drift from S into N over (several times) some characteristic distance ξ_n, the coherence length in N [12]. For the critical current I_c of an SNS junction, he derived the expression

$$I_c \approx \frac{\pi}{2eR_n}\frac{\Delta_i^2}{kT_c}\frac{d}{\xi_n}e^{-d/\xi_n}, \tag{1}$$

where R_n is the resistance of the junction in its normal state, Δ_i is the superconducting gap at the normal interlayer interface, T_c is the bulk critical temperature of S electrodes, and d is the thickness of N layer. The expressions for ξ_n are simple in the two limiting cases in the ratio of ξ_s, the superconducting coherence length in S, and l_n, the mean-free path in N; in the "clean limit" $\xi_s \ll l_n$, one has $\xi_{nc} = \hbar v_n/2\pi kT$, where v_n is the Fermi velocity in N, while in the "dirty limit" $l_n \ll \xi_s$, this changes to $\xi_{nd} = \sqrt{\hbar v_n l_n/6\pi kT}$. This simple theory allows for some striking predictions. First, the critical current should die off exponentially as d is increased. Second, if d is fixed, I_c should also exponentially decay as the temperature is increased. These are the key experimental signatures of a true SNS junction. Subsequently, more accurate formulas have been derived from microscopic considerations [14], but the original theory of De Gennes did capture the essential physics, and the corrections are usually not large. The formula (1) and the above statements apply also to an $SN'S$ junction in which the N' layer is superconducting itself below T_c', for $T_c' < T < T_c$, but in this case the expressions for ξ_{nc} and ξ_{nd} get more involved [16].

Assuming that the above conceptual framework is extendable to HTS compounds, and given that ξ_s and l_n are both very short in cuprates as well as in all other oxide barriers under study, one would predict ξ_n to be rather short in HTS-based Josephson junctions at temperatures of interest (more details below). Hence, Josephson coupling across thick oxide barrier layers should not be possible, in particular, in the c-axis geometry.

On the experimental side, a thorough analysis of data from many groups revealed that HTS junctions of different types (step edge, grain boundary, etc.) show great and unexpected similarity [16]. This specifically includes an almost ubiquitous linear decrease in j_c with increasing temperature, which is not expected in true SNS junctions. Delin and Kleinsasser [16] concluded that this indicated a common problem—existence of microshorts, i.e., superconducting filaments connecting the electrodes. In some cases, these were even directly observed by cross-section transmission electron microscopy; in other cases, their presence was inferred from rough film morphology, growth spirals, presence of secondary-phase precipitates, rough interfaces formed at grain boundaries or by etching, etc. If $PrBa_2Cu_3O_7$ (PBCO) is used for the barrier, there is an additional potential problem: superconductivity with $T_c = 80$ K has been observed in some PBCO single crystals, so one could suspect that superconducting islands might exist inside PBCO barriers. Moreover, some recent junction studies directly contradict earlier findings. Bari *et al.* [17] found that a $La_{0.7}Ca_{0.3}MnO_3$ barrier com-

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pletely blocks supercurrent, even when it was very thin—an order of magnitude thinner then in Refs. [6,7]. Barholz *et al.* [18] observed no supercurrent in coplanar junctions with trenches down to 50 nm; they ascribed previous findings [4,5,10] to HTS microshorts formed by inadvertent resputtering of $YBa_2Cu_3O_7$ (YBCO). Yoshida [19] revisited *ab*-plane step-edge junctions with YBCO electrodes and Co-doped PBCO as the barrier; he found that $\xi_n = 6$ Å, which is 2 orders of magnitude less than what was claimed before.

In our judgment, one could make the most compelling case for GPE using trilayer (sandwich) junctions, provided that the films are synthesized free of any secondary-phase precipitates and with atomically smooth interfaces; the rms surface roughness should be much smaller than the barrier thickness. Few such junctions were fabricated [20] by molecular beam epitaxy (MBE); the top and the bottom electrodes were made of Bi-2212, while a 123-Å-thick layer of Bi-2201 served as the barrier. The junctions indeed showed $T_c > 50$ K, over 3 times higher than $T_c \approx 15$ K in the single-phase Bi-2201 film [20].

Subsequently, at Oxxel we have developed a technology [21–23] to deposit atomically smooth films and multilayers with a substantial yield and to fabricate uniform junctions and arrays. Thus we were in a good position to reexamine GPE, by repeating, expanding, and improving upon the above experiments. Here we report on a group of a few dozen HTS trilayer films, with several hundred junctions fabricated and tested. The typical device geometry is illustrated in the inset of Fig. 1. For the superconducting (S) electrodes, we used $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) with $T_c \approx 45$ K; the normal-metal (N') barriers were made of underdoped La_2CuO_{4+d} (LCO) with typical $T_c' \approx 25$ K. Such devices behaved as superconductor–normal-metal–superconductor ($SN'S$) Josephson junctions for $T_c' < T < T_c$. The barrier thickness ranged from 1 to 15 unit cells of LCO, i.e., up to $d = 200$ Å. The results shown in what follows are characteristic of this entire set of films and devices.

In the main panel of Fig. 1, we show j-V characteristics of ten such devices from a single chip, at $T = 6.4$ K. The curves are nearly the same, indicating good scaling of I_c and R_n with the junction area and excellent device uniformity. In Fig. 2, we show the $j_c(T)$ dependence. In Fig. 3, we show how such a junction responds, above T_c' of the barrier, to microwave radiation capacitively coupled from a radiative antenna—a coaxial cable with open central electrode placed very close (less than 1 mm $\ll$ the radiation wavelength) to the junction. Clear and sharp Shapiro steps are seen at the voltages given by $V = nh\nu/2e$, for $n = 1, 2, 3, \ldots$, as expected from a single Josephson junction. As the high-frequency power was increased, the step height showed oscillatory

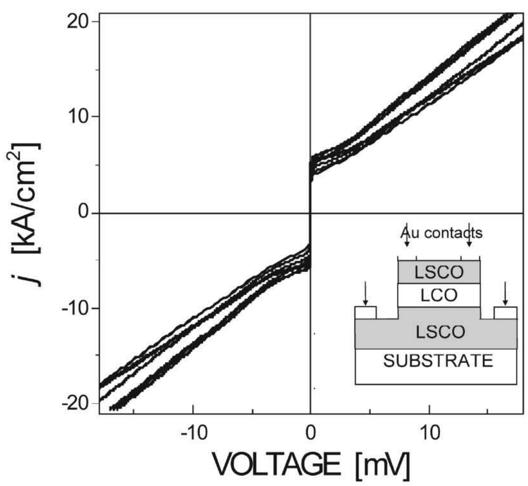

FIG. 1. Trilayer $SN'S$ devices studied in this work and their transport characteristics. Inset: The device geometry. The top and bottom HTS electrodes were made of LSCO. The barriers were made of LCO, and their thickness was varied from 13 to 200 Å. The circular mesa diameter was varied from 10 to 80 mm. Gold contacts allowed for 4-point contact transport measurements. Main panel: The current density as a function of voltage dependence (the j-V characteristics), at $T = 6.4$ K, for a set of ten sandwich junctions on the same chip. The plot illustrates very good device uniformity; in the best such set, the 1-σ spread in j_c was merely 2.5%. In the particular set shown here, the LCO barrier was 100 Å thick.

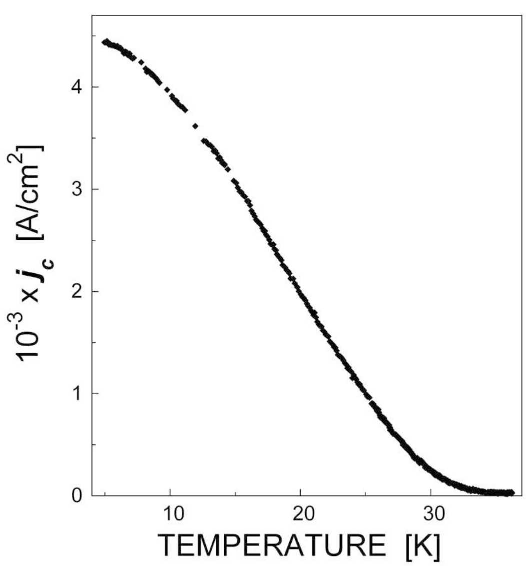

FIG. 2. The temperature dependence of critical current density of $SN'S$ trilayer junctions shown in Fig. 1. (The diameter of circular mesa was 20 μm in this particular junction, but j_s in other junctions in this set did not differ by more than a few percent.) As the temperature was raised, the I-V characteristics gradually changed from flux-flow–like (large junction, inhomogeneous current flow) at low temperature, to resistively shunted junctionlike (small junction, homogeneous current flow) at high temperature close to T_c of the LSCO electrodes.

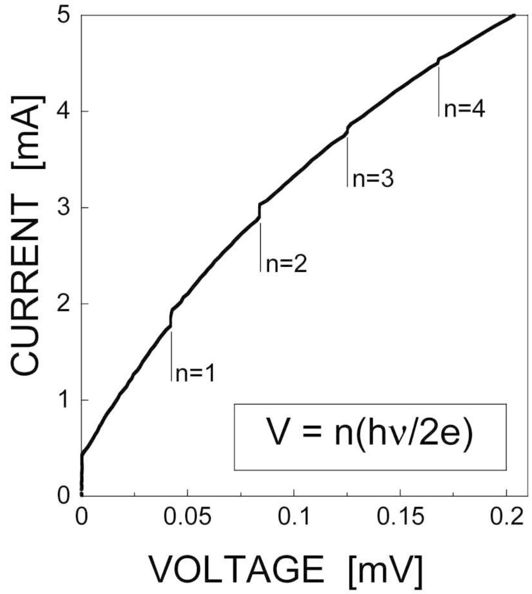

FIG. 3. Shapiro steps induced by microwave ($\upsilon = 20$ GHz) radiation in the device shown in Fig. 2, at $T = 30$ K. (Note that the voltage scale is a hundred times smaller than in Fig. 1.) The steps occur exactly at the voltages given by $V = nh\upsilon/2e$, for $n = 1, 2, 3, 4, \ldots$, as expected from a single Josephson junction. We have also observed the expected scaling of the step height with the power of microwave irradiation, and, in few cases, nearly complete modulation of j_c by the applied external magnetic field, with minima that corresponded well to the nominal junction area.

behavior, particularly clearly for the first step, in qualitative agreement with the expected Bessel-function dependence.

Additional evidence for absence of pinholes and microshorts is as follows. The trilayer film grew atomically smooth, as indicated by reflection high-energy electron diffraction during growth, and was verified directly by atomic force microscopy and x-ray diffraction afterwards [21]. Indeed, except for little doping, LSCO is almost the same compound as LCO, and we have a quasi-homoepitaxy; this provides for very smooth interfaces. But the most direct proof comes from a reversible barrier (de)oxygenation process [21] that we utilized extensively to attest the barrier integrity. Annealing such a junction at low temperature in vacuum renders LCO insulating, while it leaves LSCO almost intact; a $SN'S$ junction is converted into a superconductor-insulator-superconductor (SIS) device. In this case, we saw [22] no supercurrent, i.e., no microshorts, even in devices with the thinnest (one unit cell thick) LCO barriers; indeed, in 15 times thicker barriers, pinholes are exponentially less probable. Hence, this is a rather solid demonstration that these devices are free of physical microshorts. One remaining (remote) possibility is that microshorts may be generated in LCO each time anew by oxygen annealing, but this is not consistent with reproducibility, uniformity, and good scaling with the area—and definitely this cannot explain the same effect in Bi-2201, where T_c' does not exceed about 15 K at any oxygen content. Actually, neutron diffraction studies [24] indicate that oxygen intercalates in stages in LCO, which may be the least disordered among the HTS compounds. Next, we have looked very carefully, using a novel technique (resonant scattering of soft-x-ray synchrotron radiation) that enhances the sensitivity by 4 orders of magnitude [25], for any signs of inhomogeneity (such as charge stripes, charge-density waves, etc.) of the free-carrier fluid in our LCO films, but have not see any, down to the 3×10^{-7} electrons level.

Overall, we consider that our data show conclusively that in HTS-based $SN'S$ junctions supercurrent can flow across a barrier 100 times thicker than the superconducting coherence length (ξ_s), the mean-free-path of the charge carriers (l_n), and the induced coherence length in N (ξ_n) as inferred from the conventional theory of the proximity effect. In other words, we assert that GPE is indeed real, at least for our choice of S and N' and in our device geometry. While in this Letter we have considered barriers up to 200 Å thick, the supercurrent was sizeable, and it is clear that the maximum coupling distance should be at least several times larger, even in our c-axis geometry—and conceivably longer in the more favorable a-axis geometry (as in Refs. [4–11]).

Analysis of our data along the lines of standard theory [12–14] fails to provide a satisfactory explanation. In conventional superconductors, ξ_n is dependent upon and limited by ξ_s and l_n [12]. In cuprates, both ξ_s and l_n are very short, and so should be ξ_n; the representative values are $\xi_n \approx 20$–40 Å for transport parallel to the CuO_2 planes, and $\xi_n \approx 1$–2 Å for transport along the c axis. Since the junction diameter is $w = 10$–80 mm, while (for $j_c = 20\ \mathrm{A/cm^2}$ at $T = 30$ K) the Josephson penetration depth is $\lambda_J \approx 100$ mm, we are in the small junction regime, $w < 4\lambda_J$, and the supercurrent flow should be homogenous. Note, however, that at lower temperature the critical current increases fast (see Fig. 2) and we cross over to a flux-flow regime; for this reason, the fit to Eq. (1) should be limited to the region near T_c where j_c is definitely not linear but strongly curves upward following approximately the $(T_c - T)^2$ dependence, as expected for soft boundary conditions [16]. While the fitting is somewhat uncertain due to the limited temperature range, clearly the inferred value of ξ_n is 2 orders of magnitude longer then expected—which merely means that the standard theory is inapplicable as is.

Next, we can rule out explanations invoking the divergence of ξ_s near T_c (at $T = 30$ K, we are about 15 K below T_c of LSCO and one gets $\xi_s(T) = 1.4\xi_{s0}$, while in Bi-2212 at $T = 50$ K, $\xi_s(T) = 1.2\xi_{s0}$; these are small corrections), the divergence in ξ_n close to T_c' (this is particularly clear in the case of Bi-2201 [20] where the operating $T \approx 50$ K is much higher than $T_c' \approx 15$ K), and the divergence in quasiparticle lifetime (this could occur well below T_c' but not above).

A remark is due here on the difference between the present work, which reports on $SN'S$ junctions, and Ref. [22], which considered SIS devices. There, we showed that the interface between HTS and the antiferromagnet Mott insulator is extremely sharp, on 1 Å scale. In contrast, once the inserted LCO barrier is doped across the metal-insulator transition and becomes HTS itself (albeit with a lower T_c'), as is the case here, the situation changes dramatically and GPE indeed takes place.

Given that the barrier is 200 Å thick, we suspect that supercurrent must be mediated by resonant tunneling through a series of energy-aligned states within the N' layer [26,27]. This process must preserve phase coherence as well as the in-plane momentum; i.e., the transmission must be (at least partially) specular. This suggests that the N' state itself may be unusual; e.g., it may contain preformed pairs, superconducting fluctuations, or droplets well above the apparent T_c' [1,2,28–30]. In this Letter, we have provided evidence that extrinsic inhomogeneity, such as grains of unwanted phases that pierce the barrier and create microshorts, can be eliminated using advanced thin-film deposition techniques, and is absent in our devices. However, some cuprates are inhomogeneous on a nanoscopic length scale, as indicated by scanning tunneling microscopy, neutron diffraction, and muon spin resonance [31–33]. This could be intrinsic; i.e., it could occur for thermodynamic reasons. In this case, such "imperfection" would be inescapable, even if the layers were atomically smooth. But if T_c in such a N' material increases significantly when it is brought in contact with HTS electrodes, one would still (for the lack of a better terminology) call this a "proximity effect"—and if the length scale is anomalously large, GPE. This would be equally useful for applications, since one would be able to use thick barriers. As for the theory, one would need to account for this strange N' phase, the way in which it transmits supercurrent well above T_c', the occurrence of the large length scale, and the dependence of j_c on d, T, H, the doping level, etc.; with some further development in the technique, such data should become accessible experimentally. It is conceivable that GPE also occurs in PBCO and/or in manganites, perhaps by a different mechanism; this also deserves additional in-depth study.

In conclusion, we have demonstrated that GPE is a real and intrinsic effect, and it is arguably the first truly unconventional property of the HTS state. This should stimulate further detailed experimental and theoretical study, in view of possible electronics applications but perhaps also to learn more about the HTS state itself.

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[1] V. Z. Kresin, Yu. Ovchinnikov, and S. Wolf, Appl. Phys. Lett. **83**, 722 (2003).
[2] G. Alvarez, M. Mayr, A. Moreo, and E. Dagotto, cond-mat/0401474.
[3] A. Saxena, A. R. Bishop, and K. A. Mueller (unpublished).
[4] U. Kabasawa *et al.*, Jpn. J. Appl. Phys. **30**, 1670 (1991).
[5] Y. Tarutani *et al.*, Appl. Phys. Lett. **58**, 2707 (1991).
[6] M. Kasai *et al.*, Jpn. J. Appl. Phys. **29**, L2219 (1990).
[7] M. Kasai *et al.*, J. Appl. Phys. **72**, 5344 (1992).
[8] R. Yuasa *et al.*, Physica (Amsterdam) **185C**, 2587 (1991).
[9] J. B. Barner *et al.*, Appl. Phys. Lett. **59**, 742 (1991).
[10] A. Meltzow *et al.*, IEEE Trans. Appl. Supercond. **7**, 2852 (1997).
[11] R. S. Decca *et al.*, Phys. Rev. Lett. **85**, 3708 (2000).
[12] P. G. De Gennes, Rev. Mod. Phys. **36**, 225 (1964).
[13] G. Deutscher and P. G. De Gennes, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2, pp. 1005–1034.
[14] K. K. Likharev, *Dynamics of Josephson Junctions and Circuits* (Gordon and Breach, New York, 1986).
[15] H. Meissner, Phys. Rev. **117**, 672 (1960).
[16] K. A. Delin and A.W. Kleinsasser, Supercond. Sci. Technol. **9**, 227 (1996).
[17] M. A. Bari *et al.*, IEEE Trans. Appl. Supercond. **7**, 2304 (1997).
[18] K.-U. Barholz *et al.*, Physica (Amsterdam) **334C**, 175 (2000).
[19] J. Yoshida, IEICE Trans. Electron. **E83-C**, 49 (2000).
[20] I. Bozovic *et al.*, J. Supercond. **7**, 187 (1994).
[21] I. Bozovic *et al.*, Phys. Rev. Lett. **89**, 107001 (2002).
[22] I. Bozovic *et al.*, Nature (London) **422**, 873 (2003).
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[24] B. O. Wells *et al.*, Z. Phys. B **100**, 535 (1996).
[25] P. Abbamonte *et al.*, Science **297**, 581 (2002).
[26] I. A. Devyatov and M. Yu. Kupriyanov, JETP Lett. **59**, 200 (1994).
[27] A. A. Abrikosov, Physica (Amsterdam) **317C**, 154 (1999).
[28] S. Doniach and M. Inui, Phys. Rev. B **41**, 6668 (1990).
[29] E.W. Carlson *et al.*, in *The Physics of Conventional and Unconventional Superconductors*, edited by K. H. Bennemann and J. B. Ketterson (Springer-Verlag, Berlin, 2002), pp. 1–180.
[30] Z. A. Xu *et al.*, Nature (London) **406**, 486 (2000).
[31] J. E. Hoffman *et al.*, Science **295**, 466 (2002).
[32] J. M. Tranquada, J. Phys. Chem. Solids **59**, 2150 (1998).
[33] T. Savici *et al.*, Phys. Rev. B **66**, 14 524 (2002).