

Degenerate Ground State in a Mesoscopic $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ Grain Boundary Josephson Junction

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We have measured the current-phase relationship $I(\varphi)$ of symmetric 45° $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ grain boundary Josephson junctions. Substantial deviations of the Josephson current from conventional tunnel-junction behavior have been observed: (i) The critical current exhibits, as a function of temperature T , a local minimum at a temperature T^* . (ii) At $T \approx T^*$, the first harmonic of $I(\varphi)$ changes sign. (iii) For $T < T^*$, the second harmonic of $I(\varphi)$ is comparable to the first harmonic, and (iv) the ground state of the junction becomes degenerate. The results are in good agreement with a microscopic model of Josephson junctions between d -wave superconductors.

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The most important phenomenological difference between the high- T_c cuprates and conventional superconductors regards the orbital symmetry of the superconducting order parameter. In the cuprates the pair potential changes sign depending on the direction in momentum space according to [1,2] $\Delta(\vartheta) = \Delta_0 \cos 2(\vartheta - \theta)$, where ϑ is the angle between the wave vector and the (laboratory) x axis, while θ is the angle between the Cu-Cu bond direction of the superconductor and the x axis. This unconventional d -wave symmetry was predicted [3] and experimentally confirmed [1,2] to be directly measurable in the Josephson effect between a high T_c and a conventional superconductor. Another consequence of the d -wave symmetry is that midgap states (MGS) with energy $\varepsilon = 0$ should form on the free surface of a d -wave superconductor if $\Delta(\vartheta)$ has opposite signs on incident and reflected electronic trajectories [4]. The MGS density must be maximal for (110)-like surfaces and this prediction has in fact been confirmed by STM microscopy on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) single crystals [5] which revealed the MGS contribution to the YBCO tunneling density of states. The presence of the MGS is expected to influence in a spectacular way also the Josephson effect in junctions between d -wave superconductors with different crystallographic orientations. Yet no clear manifestation of the MGS in the Josephson effect in such junctions has been observed so far, which is a challenge for the concept of d -wave superconductivity in the cuprates.

Moreover, due to possible applications in quantum computing [6,7], there is substantial interest in Josephson junctions and circuits with a doubly degenerate ground state. Such a state was predicted in an asymmetric 45° junction ($\theta_1 = 0^\circ$ and $\theta_2 = 45^\circ$, the angles $\theta_{1,2}$ are defined in Fig. 1), since odd harmonics of the Josephson current

$I(\varphi) = \sum_n I_n \sin n\varphi$ are suppressed by symmetry [8,9]. The current-phase relation observed in Ref. [10] indeed showed a substantial contribution of the second harmonic I_2 . However, there is a finite supercurrent flowing along the interface in the ground state of asymmetric 45° junctions [9]. Therefore they do not lead to completely quiet qubits in the sense of Ref. [6].

Motivated by the search for both, the MGS in high- T_c Josephson junctions and a quiet qubit, we have studied symmetric 45° junctions (i.e., junctions with $\theta_1 = -\theta_2 = 22.5^\circ$). In this paper we report the first direct observation of several effects exclusive to such junctions: temperature controlled sign change of the first harmonic of the Josephson current, a nonmonotonic temperature dependence of the critical current, and the development of a doubly degenerate ground state of the system.

Let us start with a description of the theoretical predictions for Josephson junctions between d -wave superconductors. In symmetric short junctions the Josephson current density is conveniently described in terms of the Andreev levels in the junction as [11]

$$j(\varphi) = \frac{k_F}{\Phi_0 d} \sum_n \int_{-\pi/2}^{\pi/2} d\vartheta \cos\vartheta f[\varepsilon_n(\varphi, \vartheta)] \frac{\partial \varepsilon_n(\varphi, \vartheta)}{\partial \varphi},$$

where φ is the superconducting phase difference between the banks, Φ_0 is the magnetic flux quantum, k_F is the Fermi momentum, d is the average separation of the CuO_2 planes, $f(\varepsilon)$ is the Fermi distribution function, and $\varepsilon_n(\varphi, \vartheta)$ is the energy of the n th Andreev level for an electron incident on the junction at an angle ϑ with respect to the boundary normal. At a given ϑ there exist only two Andreev levels with energies $\pm\varepsilon(\varphi, \vartheta)$.

The nature of the Andreev levels changes with the impact angle ϑ : (i) For $22.5^\circ < |\vartheta| < 67.5^\circ$, MGS are formed at $\varphi = 0$ whose energy is split by a finite phase difference φ across the contact. In this range of impact angles $\varepsilon(\varphi)$ can be qualitatively described by $\varepsilon_{\text{MGS}}(\varphi) = \Delta(\pi/4) \sin(\varphi/2) \sqrt{\mathcal{D}(\pi/4)}$, where $0 \leq \mathcal{D}(\vartheta) \leq 1$ is the angle-dependent barrier transparency [12]. (ii) For $|\vartheta| < 22.5^\circ$ and $67.5^\circ < |\vartheta| < 90^\circ$, no MGS are formed at $\varphi = 0$ and the Andreev levels resemble those formed in a Josephson junction between s -wave superconductors. In this range of impact angles $\varepsilon(\varphi)$ can be qualitatively described by $\varepsilon_{\text{conv}}(\varphi) = \Delta(0)[1 - \mathcal{D}(0)\sin^2(\varphi/2)]^{1/2}$.

When inserted into the equation for $j(\varphi)$, the two sets of Andreev levels yield contributions of opposite sign to the Josephson current, $I(\varphi) = I_{\text{MGS}}(\varphi) + I_{\text{conv}}(\varphi)$. Close to T_c , when $T \gg \Delta_0(T)$, we can approximately write $I_{\text{conv}} \propto \mathcal{D}(0)(\Delta_0^2/T)\sin\varphi$ and $I_{\text{MGS}} \propto -\mathcal{D}(\pi/4)(\Delta_0^2/T)\sin\varphi$. For a sufficiently large ratio $\mathcal{D}(0)/\mathcal{D}(\pi/4)$ the sign of the first harmonic at high temperatures is therefore given by the conventional contribution. Lowering the temperature to $\sqrt{\mathcal{D}(\pi/4)}\Delta_0(T) \ll T \ll \Delta_0(T)$, I_{conv} saturates to $I_{\text{conv}} \propto \mathcal{D}(0)\Delta_0\sin\varphi$, whereas $|I_{\text{MGS}}|$ continues to grow according to $I_{\text{MGS}} \propto -\mathcal{D}(\pi/4)(\Delta_0^2/T)\sin\varphi$. As a result, near $T^* \sim \Delta_0\mathcal{D}(\pi/4)/\mathcal{D}(0)$ the first harmonic will change sign and therefore the second harmonic will dominate the current, leading to a doubly degenerate ground state.

In a symmetric junction $\varepsilon(\varphi, \vartheta) = \varepsilon(\varphi, -\vartheta)$ [12] and therefore the total current along the interface is exactly zero at any T and φ , contrasting with a finite total current in an asymmetric junction. A more detailed analysis shows that in symmetric junctions time reversal symmetry is broken and small currents of equal magnitude and opposite sign flow along the interface in the left and the right superconducting banks. Thus, although they are much closer to being quiet than asymmetric junctions, even the symmetric junctions are not completely quiet.

An experimental confirmation of the above theoretical predictions requires the use of mesoscopic junctions. In fact, since the grain boundaries are faceted on a length scale $\sim 0.1 \mu\text{m}$ [13], $I(\varphi)$ of macroscopic junctions necessarily represents a nontrivial average over junctions with different misorientations. However, standard transport measurements of the critical current $I_c = \max_{\varphi}\{I(\varphi)\}$ are possible only at temperatures smaller than the energy of the grain boundary Josephson junction, $\sim \Phi_0 I_c / 2\pi$. Therefore we have used the modified Rifkin-Deaver method [14,15] which offers a unique possibility to study $I(\varphi)$ at temperatures T much higher than the junction energy. This is achieved by connecting the banks of the junction to form a superconducting ring (or an rf SQUID) so that the phase difference across the junction is controlled by the (large) phase stiffness of the ring.

The YBCO thin films of thickness 100 nm were prepared by laser deposition on 45° symmetric bicrystal substrates. The rf SQUIDS were patterned in the shape of a square washer $3500 \mu\text{m} \times 3500 \mu\text{m}$ with

a hole $50 \mu\text{m} \times 50 \mu\text{m}$ by electron beam lithography (see Fig. 1). Here we present the data on two samples with critical current densities $j_c \approx 2.6 \times 10^3 \text{ A/cm}^2$ for sample No. 1 and $j_c \approx 400 \text{ A/cm}^2$ for sample No. 2. The estimated Josephson penetration depth λ_J is much smaller than the width of the wide junction, $w_l = 1725 \mu\text{m}$, and larger than the width of the narrow junction, $w_s = 0.7 \mu\text{m}$ and $w_s = 0.5 \mu\text{m}$, for samples No. 1 and 2, respectively. Thus the behavior of the rf SQUID is dictated by the narrow junction only. The submicron bridge was formed at a position between the defects of the substrate which are visible in Fig. 1.

In the modified Rifkin-Deaver method [14,15], the sample is inductively coupled to a high-quality parallel resonance circuit ($Q = 155$ and 165 for samples No. 1 and 2, respectively) driven at its resonant frequency ω_0 . The angular phase shift α between the driving current and the voltage across the circuit is measured by a rf lock-in voltmeter as a function of the external magnetic flux Φ_{dc} , which is conveniently measured in the dimensionless units $\varphi_{dc} = 2\pi\Phi_{dc}/\Phi_0$. The phase difference across the junction φ was calculated from the $\alpha(\varphi_{dc})$ data using the coupling coefficient between the rf SQUID and the tank coil $k^2 = 2.6 \times 10^{-3}$ and 3.6×10^{-3} for samples No. 1 and 2, respectively. After inverting the $\varphi = \varphi(\varphi_{dc})$ function, $I(\varphi)$ can be obtained from $\beta f(\varphi) = \varphi_{dc}(\varphi) - \varphi$, where $f(\varphi) = I(\varphi)/I_c$, $\beta = 2\pi LI_c/\Phi_0$, and $L = 80 \text{ pH}$ is the inductance of the rf SQUID. The details of the experimental method are given elsewhere [15].

The measured $\alpha(\varphi_{dc})$ curves shown in Fig. 2 exhibit local minima at low T when φ_{dc} is a multiple of 2π . This is qualitatively different from what has been observed before for 45° symmetric grain boundary Josephson junctions on samples with $w_s > 1 \mu\text{m}$ where no such minima were found [16]. We believe that the difference is caused by the existence of the bicrystal boundary defects with a typical

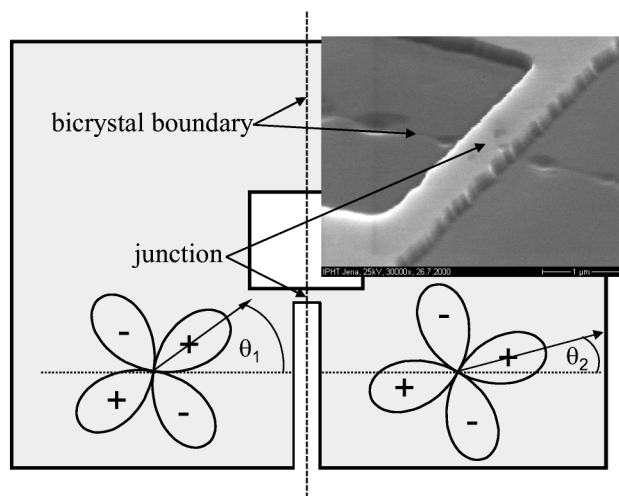


FIG. 1. Schematic picture of the rf SQUID. The YBCO thin film occupies the gray area. The inset shows an electron microscope image of the narrow grain boundary Josephson junction.

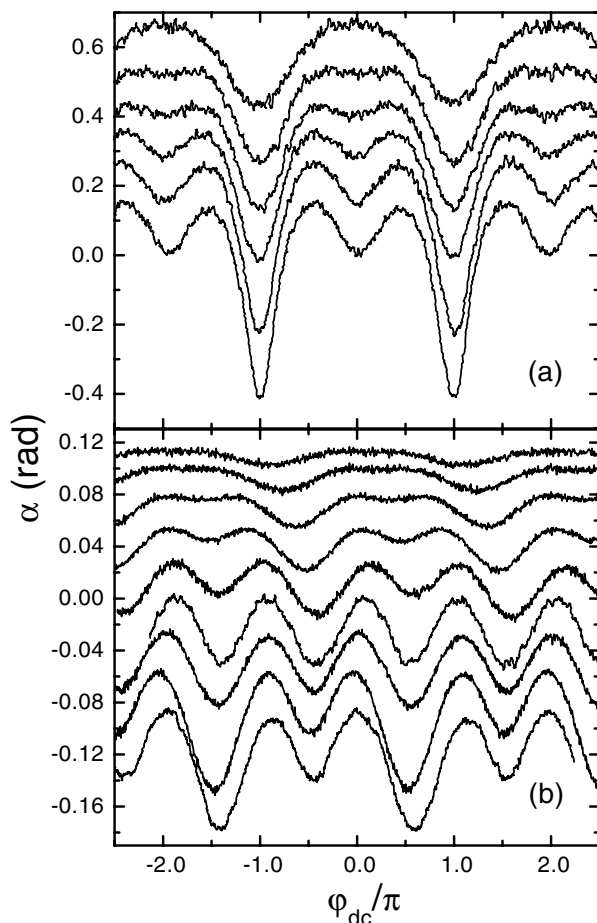


FIG. 2. The phase angle α as a function of φ_{dc} measured at different temperatures for samples No. 1 (a) and No. 2 (b). From top to bottom, the data correspond to (a) $T = 30, 20, 15, 10, 4.2,$ and 1.8 K and (b) $T = 35, 30, 25, 20, 15, 11, 10, 5,$ and 1.6 K. The data are vertically shifted for clarity.

distance $\sim 1 \mu\text{m}$ (see Fig. 1), which cannot be avoided for large junctions.

The Josephson current calculated from the measured $\alpha(\varphi_{dc})$ data is shown in Fig. 3. Note the anomalous form of $I(\varphi)$ at low temperatures. The anomalies in sample No. 2 are much more pronounced than in sample No. 1. We believe this is a combined effect of smaller junction cross sections and higher junction quality, as evidenced by the much smaller values of I_c in sample No. 2. In Fig. 4 we plot the first two harmonics I_1 and I_2 for the sample No. 2. The most striking result is that for $T^* \approx 12$ K, I_1 changes sign. In the same temperature region where I_1 starts to exhibit a downturn, the value of $|I_2|$ rises from the negligible high- T values to values comparable to $|I_1|$ at low T , suggesting a common origin of both phenomena. Furthermore, Fig. 4 shows that close to T^* , there is a local minimum of the critical current I_c as a function of T , which is associated with the sign change of I_1 . These results are in a qualitative agreement with theoretical predictions for $I(\varphi)$ of 45° junctions with ideally flat interfaces [8,17].

We can reconstruct the free energy F of the junction as a function of φ from $F(\varphi) = (\Phi_0/2\pi) \int_0^\varphi d\phi I(\phi)$. The

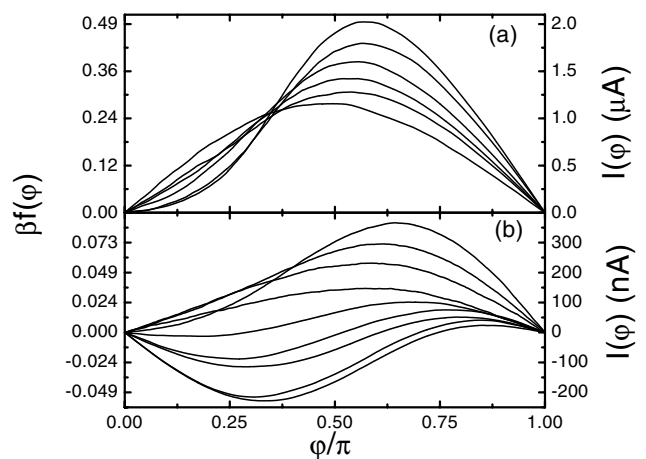


FIG. 3. $I(\varphi)$ for samples No. 1 (a) and No. 2 (b). From top to bottom at $\varphi/\pi = 0.5$, the data correspond to (a) $T = 30, 20, 15, 10, 4.2,$ and 1.8 K and (b) $T = 20, 25, 30, 35, 15, 11, 10, 5,$ and 1.6 K. The data in Fig. 3b corresponding to $T = 20, 25, 30,$ and 35 K were multiplied by a factor 4 for clarity.

result is shown in Fig. 5. Note that for $T \leq 15$ K, the free energy minimum of the sample No. 2 moves away from $\varphi = 0$, and the $F(\varphi)$ curve exhibits two degenerate minima at $\varphi = \pm\varphi_0$, as observed previously in Ref. [10] on asymmetric 45° junctions; see Fig. 5.

In Fig. 4 we compare the experimental data with a theoretical treatment based on the quasiclassical Eilenberger equations which was introduced in the s -wave case in Ref. [18] and will be described in detail elsewhere. Within our approach the junction is described by two phenomenological parameters, the junction transparency \mathcal{D} and the roughness parameter $0 < \rho < \infty$. The temperature dependence of I_1 , I_2 , and I_c is fit well by our theory with $\mathcal{D} = 0.3$ and $\rho = 0.3$. The theoretical j_c is reported in

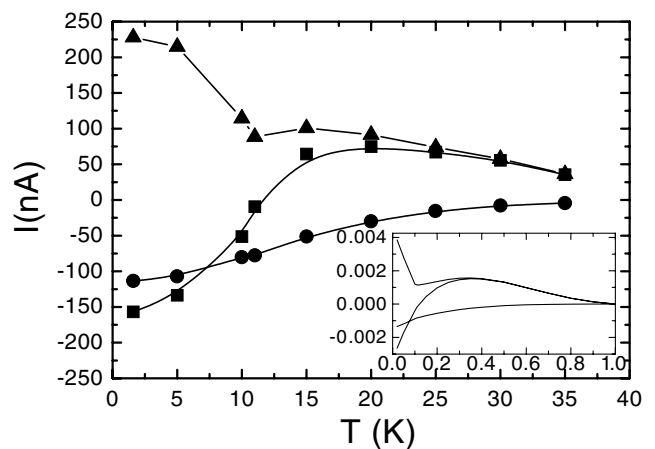


FIG. 4. The critical current I_c (triangles) and the harmonic components I_1 (squares) and I_2 (circles) of the Josephson current as a function of temperature for sample No. 2. The figure is obtained by the Fourier analysis of $I(\varphi)$ shown in Fig. 3b. Inset: Theoretical prediction for the temperature dependence of j_c , j_1 , and j_2 for a junction with $\mathcal{D} = 0.3$ and $\rho = 0.3$. The current densities are plotted in units of the Landau critical current density; the temperature is in units of T_c .

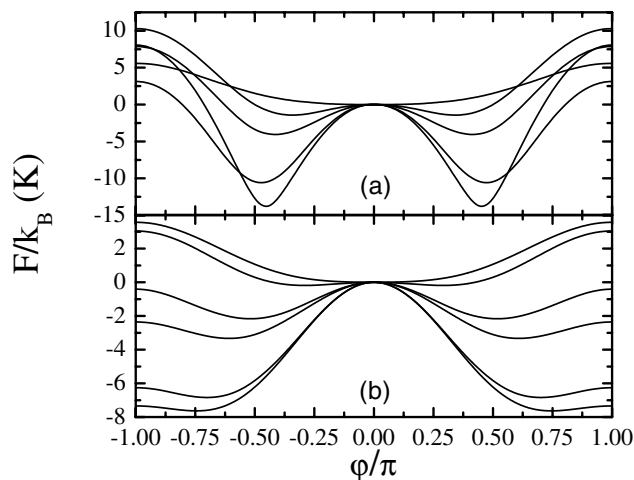


FIG. 5. Free energy $F(\varphi)$ as a function of the phase difference across the weak link. The zero of energy has been set so that $F(0) = 0$. (a) Asymmetric 45° grain boundary (Ref. [10]). Top to bottom curves correspond to $T = 30, 20, 15, 10,$ and 4.2 K, respectively. (b) Symmetric 45° grain boundary (present work). Top to bottom curves correspond to $T = 20, 15, 11, 10, 5,$ and 1.6 K, respectively.

Fig. 4 in units of the Landau critical current density $j_0 = k_F \Delta_0 / \Phi_0 d$, where Δ_0 is the gap parameter at the interface. The experimental critical current density j_c for 45° junctions is smaller than j_c^{bulk} by a factor [13] $\sim 10^{-5} - 10^{-4}$. Remarkably, the absolute value of j_c is also well described by $\mathcal{D} = 0.3$ and $\rho = 0.3$. In fact, in 45° junctions Δ_0 can be estimated from [13] $\Delta_0 \sim I_c R_N \sim 10^{-1} - 1$ meV, and therefore $j_0 / j_c^{\text{bulk}} \sim \Delta_0 / \Delta_0^{\text{bulk}} \sim 10^{-2} - 10^{-1}$. Together with the theoretical result $j_c / j_0 \sim 10^{-3}$, this explains the experimental ratio j_c / j_c^{bulk} .

Before concluding let us point out that a large I_2 can be expected also in a real-space scenario, in which it is postulated that due to surface roughness and/or twinning of the superconducting banks, spontaneous magnetic flux is generated along the interface [19,20]. We are not aware of any prediction of a sign change of I_1 within the real-space scenario. But we can rule it out also in a different way, on very general grounds: I_2 corresponds to a term $-F_2 \cos 2\varphi$ in the junction free energy, where $F_2 = (\Phi_0 / 4\pi) I_2$. In the real-space scenario, F_2 is the free energy gain due to the formation of spontaneous magnetic flux along the junction. Taking $I_2 \approx 120$ nA for the sample No. 2 at low T , we estimate $F_2 / k_B \approx 1.3$ K. However, since the associated pattern of phase difference fluctuations along the junction is not controlled by the external circuit (unlike the average phase difference across the junction), thermal fluctuations would smear the I_2 component at $T > F_2 / k_B$, in disagreement with experiment.

In conclusion, we have found that symmetric 45° junctions exhibit doubly degenerate ground states. Therefore they are of potential use in superconducting qubit fabrication. The qubits based on asymmetric 45° junctions are not quiet [6], since there exists spontaneously generated flux along the interface [21] which should change sign between the two different ground states of the junction. The qubits based on symmetric junctions might be close to being completely quiet, since their spontaneously generated flux is unmeasurably small [21]. The key technological question is how to increase the energy barrier between the two degenerate minima at $\varphi = \pm\varphi_0$. An interesting possibility seems to be to increase the barrier transparency by an appropriate doping of the grain boundary [22].

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