Observation of Surface-Induced Broken Time-Reversal Symmetry in $YBa_2Cu_3O_7$ Tunnel Junctions

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Data from *ab*-oriented $YBa_2Cu_3O_7$/I/Cu tunnel junctions are presented. Self-assembled monolayers form the insulating tunnel barrier, I. The $YBa_2Cu_3O_7$ features in the tunneling conductance match those of low-leakage *ab*-oriented $YBa_2Cu_3O_7$/Pb junctions. Results show that the zero-bias conductance peak is an Andreev bound state (ABS) of a *d*-wave order parameter. In *zero* magnetic field, the ABS splits below ~ 7 K, consistent with the presence of a subdominant order parameter at the surface. An applied magnetic field induces further splitting that grows nonlinearly with increasing field. [S0031-9007(97)03529-1]

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Tunneling spectroscopy provides unsurpassed sensitivity and resolution in the measurement of the superconducting quasiparticle density of states, yielding information on the superconducting mechanism and gap [1]. However, the $YBa_2Cu_3O_7$ (YBCO) features reproducibly observed in the conductance of $YBa_2Cu_3O_7$/Pb tunnel junctions are quite puzzling because they are qualitatively different than those expected for a conventional superconductor [2–6]. One particularly intriguing feature is the zero bias conductance peak (ZBCP) observed when tunneling into *ab*-oriented thin films [2–5]. This feature was originally analyzed in terms of spin-flip scattering of the tunneling electrons from magnetic impurities speculated to exist in the insulating barrier [3]. The temperature and voltage dependence of the ZBCP and its splitting upon application of a magnetic field showed some qualitative agreement with this model [7,8]. However, quantitative analysis showed major discrepancies. According to the spin-flip scattering model, the splitting of the ZBCP is linear with field and proportional to the Landé g factor of the scattering centers. In *ab*-plane YBCO tunneling, the ZBCP splitting is nonlinear with field, and its magnitude implies an anomalously large g factor [3]. A further observation that challenges the spin-flip scattering analysis for YBCO is the absence of the ZBCP in the tunneling conductance of *c*-axis-oriented YBCO/Pb junctions.

Zero-bias quasiparticle bound states in the tunneling density of states of *p*-wave superconductors have been proposed [9]. For the same physical reason, Hu [10] showed that a quasiparticle bound state forms at the Fermi energy (defined to be zero) when the node of a *d*-wave order parameter [11] is normal to a specularly reflecting surface, regardless of any proximity effects. Quasiparticles reflecting from the surface experience a change in the sign of the order parameter along their trajectory and subsequently undergo Andreev reflection. Constructive interference between incident and Andreev reflected quasiparticles leads to bound states confined to the surface. These bound states can carry current and will produce a ZBCP in a tunneling spectrum [12–14]. Further calculations have considered $d_{x^2-y^2}$ symmetry gaps at surface orientations ranging from (100) to (110). These have shown that the Andreev bound state is a robust feature existing for any specular surface misoriented from (100) (the lobe direction of the $d_{x^2-y^2}$ gap), albeit with variable spectral weight [12,13,15]. In a broken time reversal symmetry (BTRS) state, the Andreev bound state shifts to finite energy, resulting in a split ZBCP [14,16].

It is generally agreed that the bulk state of YBCO does not exhibit BTRS [17]. However, a state with two order parameters with a $\pi/2$ relative phase difference has been proposed to exist at the surface of YBCO, giving rise to BTRS [18]. The phase diagram of this BTRS state has recently been calculated by Fogelström *et al.* [14] who discuss the origin of a surface-induced BTRS state and make several predictions in quantitative agreement with our measurements. The essence of their theory follows: Andreev scattering near the surface of a $d_{x^2-y^2}$ superconductor causes strong pair breaking. The quasiparticles may then be paired by a subdominant pairing interaction that is less sensitive to surface pair breaking than the dominant d wave. Calculations minimizing the free energy show that the d-wave and subdominant order parameters can coexist with a $\pi/2$ relative phase difference at low temperature. This phase difference between the two order parameters leads to a spontaneous supercurrent, and a surface phase transition to a BTRS state is achieved. The bound states are shifted to finite energy in *zero* applied magnetic field. Application of an external magnetic field to the spontaneous BTRS state will further shift the bound state energy *nonlinearly* with increasing field. The predicted splitting of the ZBCP in *zero* magnetic field and its evolution with increasing field distinguishes the BTRS state. Furthermore, this zero field splitting is a unique feature of the Andreev bound state that is incompatible with spin-flip scattering.

In this Letter, we present the results of reproducible measurements of YBCO/insulator/Cu planar tunnel junctions in which the ZBCP is observed to split in *zero* magnetic field at low temperature. The measured temperature dependence of the ZBCP gives good quantitative agreement with the calculated phase diagram for surface-induced BTRS phases of a $d_{x^2-y^2}$ superconductor [14]. The observed nonlinear evolution of the ZBCP splitting with increasing magnetic field is also in agreement with these calculations.

The tunnel junctions measured in this experiment are fabricated on YBCO thin films grown by off-axis magnetron sputter deposition that typically exhibit zero resistance at $T_c = 89$ K. Four different film orientations are grown, with details of the deposition conditions published elsewhere [4,19]. After a film is grown, it is soaked in a 1 mM dry acetonitrile solution of 1,12 diaminododecane for $2\frac{1}{2}$ days. This method results in the formation of a densely packed monolayer of 1,12 diaminododecane on the YBCO surface. Although these particular films have not been extensively characterized, this general type of organic monolayer/YBCO structure has been extensively studied and characterized [20,21]. Notably, this is the first use of such structures for preparing tunnel junctions on a cuprate superconductor. The Cu counter electrodes are subsequently evaporated through a stainless steel shadow mask. The resulting tunnel junctions typically have an area of $\sim$0.2 mm^2 and a resistance that varies between 4 and 100 Ω. Note that although tunnel junctions are formed, the state of the organic monolayer in the fabricated junction is not yet known.

Conventional I-V and dI/dV-V tunneling measurements are performed in a standard four-lead arrangement as a function of temperature and magnetic field. No attempts are made to shield the $\sim$1 G field of the Earth, but this field is insignificant compared to the $\sim$0.1 T field required to produce a measurable ZBCP splitting. The junctions are nominally aligned so that the magnetic field is parallel to the film's surface. However, this alignment is imprecise, and it is expected that demagnetization effects produce a diamagnetic signal perpendicular to the junction.

For YBCO/Pb junctions, the observation of the well-known Pb superconducting density of states is used to verify that elastic tunneling is the dominant transport mechanism through the junction. Since Cu has a featureless density of states, more indirect, though no less rigorous, means are required to characterize transport through the YBCO/Cu junctions. These are the observation of YBCO tunneling characteristics and the measurement of the junction resistance versus temperature. First, the YBCO/Cu junctions exhibit all the usual features attributable to the YBCO electrode that are observed in low-leakage *ab*-oriented-YBCO/Pb tunnel junctions [3,4]. These YBCO features are so well characterized that they are a strong indication that tunneling is the transport current and that it is directed predominantly along the copper oxide planes. Second, the junction resistance is almost independent of temperature. As a typical example, the resistance of a junction biased at 80 mV increases by only 4% from 77 to 4.2 K. This is consistent with the behavior of low-leakage YBCO/Pb junctions and in agreement with the expected behavior of a tunnel junction with a high barrier. Taken together, these reproducible observations provide strong support that elastic tunneling is the dominant transport mechanism through the junctions.

Typical conductance data from a YBCO/Cu junction are shown in Fig. 1. No significant anisotropy is observed between (100)-, (110)-, and (103)-oriented YBCO films, just like YBCO/Pb junctions. In addition, *ab*-plane characteristics are observed in junctions fabricated on chemically modified (001)-oriented films. We believe this indicates deeper penetration of the counter electrode material into chemically modified YBCO films compared to junctions fabricated by Pb deposition on unmodified films. This would allow tunneling current to flow in the direction of the copper oxide planes in junctions fabricated on nominally c-axis films.

The YBCO/Cu junctions exhibit a gaplike feature (GLF) at the same energy as that measured in *ab*-oriented YBCO/Pb junctions, ~ 16 meV $= 2.1 k_B T_c$. The GLF energy has also been shown to scale with T_c in *ab*-oriented Pr-doped YBCO thin films from $T_c = 90$ to 20 K, proving that the superconducting state is being probed when tunneling in the *ab*-plane direction [5]. Without such proof, the relation of the ZBCP to the Andreev bound state is suspect.

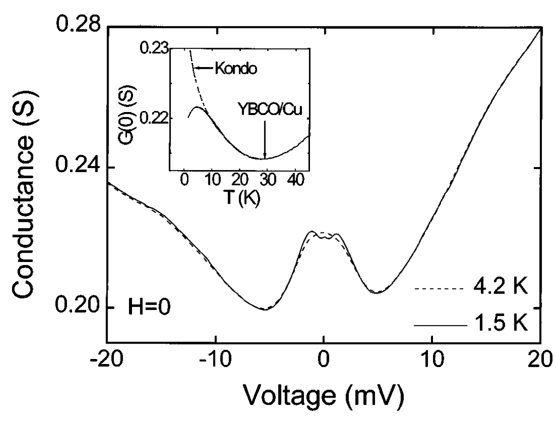

FIG. 1. Temperature-dependent conductance data from a YBCO/Cu tunnel junction. The conductance exhibits the same GLF and ZBCP observed in low-leakage *ab*-oriented-YBCO/Pb tunnel junctions. The ZBCP is observed to split in zero magnetic field at low temperature. Voltage is defined to be the voltage of Cu with respect to YBCO. Inset: Zero bias conductance, $G(0)$, versus temperature for the same junction, also in zero field. The downturn in $G(0)$ at low temperature corroborates the observation of zero field splitting and is in striking contrast to the $G(0) \sim \ln(T)$ behavior expected from Kondo-type spin-flip scattering, which is indicated by the dotted line.

The YBCO GLF is significantly different from the gaps observed in conventional low-T_c superconductors. It appears that there is a large amount of pair breaking in YBCO near the tunnel junction, resulting in a large number of states within the GLF, as expected for a d-wave order parameter. It is further significant to note that the depth of the GLF in YBCO/Cu junctions is typically twice as small as that measured in YBCO/Pb junctions. This smaller gap depth is also reproducibly observed in ab-oriented Pr-doped YBCO/Pb junctions [5], suggesting that it may be an indication of more disorder and quasiparticle scattering near the interface of YBCO/Cu junctions compared to YBCO/Pb junctions [22].

The most significant experimental observation is the temperature dependence of the ZBCP: It is reproducibly observed to split in zero magnetic field at low temperature, as presented in Fig. 1. To our knowledge, Geerk *et al.* [2] provide the only other possible evidence for a zero field ZBCP splitting in ab-oriented YBCO tunneling. Corroborating evidence comes from the zero-bias conductance, $G(0)$, versus temperature, shown in the inset to Fig. 1. Below about 30 K, the ZBCP begins to appear in the conductance with a concomitant increase in $G(0)$. The $G(0)$ increases with decreasing temperature until the onset of splitting in the density of states, below which it decreases.

Numerical simulations of thermal broadening on the low temperature data show that the conductance cannot be explained by thermal population effects alone, implying that the density of states is temperature dependent. There is a distinct splitting in the density of states below a particular temperature. The peak-to-peak separation at low temperature and the onset of the zero field splitting in the density of states are junction dependent. The peak-to-peak separation at 1.5 K is observed to range from 1.75 to 2.31 mV, and the onset temperature, T_s, of the zero field splitting varies from ~6 to ~8 K, respectively. The T_s is identified as the temperature where $G(0)$ deviates from either $\ln(T)$ or T^{-1} behavior, which is the expected functional temperature dependence for ZBCP's originating from spin-flip scattering or an Andreev bound state, respectively. The T_s is roughly the same regardless of the choice of the functional temperature dependence. Note that, due to thermal broadening effects, two peaks in the conductance are only resolved well below T_s, but the onset of splitting in the density of states manifests itself in the downward deviation of $G(0)$ and the broadening beyond $3.5k_BT$ of the region where G deviates from $\sim\ln(V)$ behavior.

As shown in Fig. 2(a), an externally applied magnetic field induces the ZBCP to split beyond its zero field value. The peak position, in energy, varies nonlinearly with increasing magnetic field, as shown in Fig. 2(b). For contrast, we also plot published experimental data representative of junctions with magnetic impurities in the insulating barrier [8,22–24]. The theoretical calculation (see below) of the magnetic field-induced ZBCP splitting is also shown in Fig. 2(b) for the case of an A_{1g}-symmetry (s wave) subdominant order parameter [14]. The theoretical peak splitting is caused by currents induced by the magnetic field and the $\pi/2$ phase difference between the two order parameters. The saturation of the splitting around ~2 T is due to the screening current saturating at the bulk critical current.

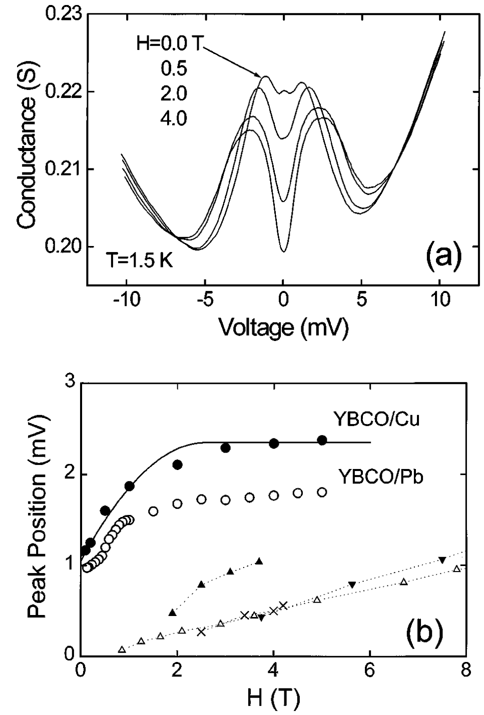

FIG. 2. (a) Magnetic field dependence of the ZBCP from a YBCO/Cu tunnel junction. A magnetic field induces further splitting of the ZBCP. (b) A compendium of data on the magnetic field-induced splitting of ZBCP's. Data from YBCO/Cu and YBCO/Pb [3] junctions are indicated by closed and open circles, respectively. The theoretical curve for the subdominant order parameter being A_{1g} (s wave) is shown as a full line [14]. As a comparison, data from other junctions with magnetic scattering centers are included. These are represented by (△) for $Ta/Ta_2O_5/Al$ [8], (▲) for $Sn/Sn_xO_y/Sn$ [23], (×) for Al/Ti-doped Al_2O_3/Al [24], and (▼) for a Au/Si:P Schottky barrier tunnel junction [25].

It is important to emphasize just how strikingly different the behavior of the YBCO ZBCP is compared to ZBCP's originating from spin-flip scattering. First, a ZBCP arising from magnetic impurity scattering will split *only* in a finite magnetic field. Figure 2(b) implies that at least 4 T is required to split paramagnetic ZBCP's by the 1.16 mV zero field value observed in the YBCO/Cu junction. Second, the magnitude of the splitting from magnetic impurities is 5 to 10 times smaller at low fields. Third, the splitting for spin-flip scattering is roughly linear and extrapolates to zero at zero field. Fourth, the zero-bias conductance increases logarithmically as the temperature approaches absolute zero, in sharp contrast to the downturn we observe. Finally, we reproducibly observe a large magnetic hysteresis in the YBCO peak position that cannot be explained by spin-flip scattering [22].

A quantitative comparison of our measured results with the calculated phase diagram of Fogelström *et al.* [14] is now presented. Maximal pair breaking and a subdominant gap with s-wave symmetry are assumed. Using our data from Fig. 1, the onset of zero field splitting in the density of states occurs at 8 ± 1 K, which corresponds to the surface phase transition temperature of the subdominant order parameter, T_s. First, we note that the measured value of T_s corresponds to the relative strength of the subdominant to dominant pairing interactions of $T_{c2}/T_{c1} \sim 0.15$, obtained for the (110) orientation with surface roughness included. This coupling strength is below the threshold value for the formation of a spontaneously broken time-reversal symmetry state in the bulk. Second, our measured value of T_s gives a calculated shift in the bound-state energy of $\delta = 1.05$ meV. We directly measure a shift of $\delta = 1.16$ meV. Any additional pair breaking due to disorder and oxygen loss near the surface is only expected to modify the predicted value of δ and T_s, but the overall agreement with theory is good. The field dependence of the tunnel splitting is also in good agreement with the theoretical predictions. Note that the splitting saturates at fields higher than H_c, the pair breaking critical field. The theoretical curve shown in Fig. 2(b) corresponds to a critical field of $H_c = 2.5$ T [14].

The presence of a GLF and ZBCP of equal strength in the tunneling conductance of (100)- and (110)-oriented films implies comparable pair breaking for both orientations. This leaves s wave as the most plausible subdominant gap symmetry, as it is much less sensitive to surface-induced pair breaking than d_{xy} or A_{2g} (g wave). The comparison of theory and experiment in Fig. 2(b) also supports this conjecture. It is also worth noting that the value of $T_{c2} \approx 12$ K is a reasonable value for an electron-phonon mechanism as the subdominant interaction. The lack of anisotropy between (100)- and (110)-oriented films, although seemingly in contradiction with an anisotropic $d_{x^2-y^2}$ gap, can be explained by surface roughness, e.g., nm-scale faceting at the interface [14]. In this model, these facets penetrate into the copper oxide planes, locally forming multiple oriented reflecting surfaces. The global film orientation then becomes a less important variable than surface faceting and scattering.

In conclusion, planar tunneling spectroscopy of the ZBCP in ab-oriented YBCO thin films reveals spontaneous surface-induced broken time-reversal symmetry. Temperature, magnetic field, and crystallographic dependencies, respectively, show that the ZBCP splits at low temperature in zero applied magnetic field, the energy of the bound state varies nonlinearly with applied magnetic field, and the ZBCP is only observed in ab-plane tunneling. These behaviors are qualitatively and quantitatively different from those expected for ZBCP's originating from magnetic spin-flip scattering of tunneling electrons and in striking agreement with the introduction of a subdominant order parameter at the surface. Finally, the ZBCP provides further direct proof that the YBCO superconducting order parameter changes sign on the Fermi surface.

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