Andreev Reflections on $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$: Evidence for an Unusual Proximity Effect

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We have measured Andreev reflections between an Au tip and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films in the in-plane orientation. The conductance spectra are best fitted with a pair potential having the $d_{x^2-y^2} + is$ symmetry. We find that the amplitude of the is component is enhanced as the contact transparency is increased. This is an indication for an unusual proximity effect that modifies the pair potential in the superconductor near the surface with the normal metal.

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The superconducting state is characterized by a pair potential (PP) $\Delta(\mathbf{r}) = V(\mathbf{r})F(\mathbf{r})$, where $V(\mathbf{r})$ is the potential representing the electron-electron interactions and $F(\mathbf{r}) \equiv \langle \Psi_\uparrow(\mathbf{r})\Psi_\downarrow(\mathbf{r})\rangle$ is the probability amplitude for finding a Cooper pair. In the case of a contact between a normal metal (N) and a superconducting metal (S), far from the interface we expect $F(\mathbf{r})$ to be zero in N and to reach a constant value in S. However, near the interface $F(\mathbf{r})$ has a nonzero value in the normal metal due to electron pairs leaking from S into N. This phenomenon is known as the proximity effect and has been studied both theoretically and experimentally for the case of superconductors with a pair potential having an s-wave symmetry [1]. Microscopically the mechanism involved in the creation of this nonzero pair amplitude $F(\mathbf{r})$ in the normal metal is a special reflection process known as Andreev reflection [2], which occurs when there is an abrupt change in the PP. Such a change occurs at a clean N/S contact, where $F(\mathbf{r})$ is continuous, due to the difference in $V(\mathbf{r})$ in the two materials. An electron approaching the superconductor (SC) from the normal metal with energy smaller than Δ cannot enter as a quasiparticle into the superconducting condensate. Instead the electron is reflected as a hole and a Cooper pair is added to the condensate. Therefore by measuring Andreev reflections one can investigate the properties of the superconducting PP.

For a perfectly transparent, small N/S contact, of size $a \ll l$, where l is the mean free path, the Andreev reflection process is manifested by a low bias ($eV \leq \Delta$) conductance which is twice as large in comparison to the high bias one. Blonder *et al.* (BTK) [3] have calculated the conductance of an N/S contact with an additional barrier represented by a delta function potential $U(x) = H\delta(x)$. They have defined a dimensionless parameter representing the barrier strength, $Z = \frac{H}{\hbar v_F}$, where v_F is the Fermi velocity. A clean N/S contact is described by $Z = 0$ and a high barrier tunneling contact by $Z \gg 1$. For finite Z values, the conductance is depressed at low bias and enhanced at $eV = \Delta$. In the case of high temperature superconductors (HTS) various experiments have indicated that the PP has a $d_{x^2-y^2}$ (d) symmetry [4], described by $\Delta(k) = \Delta_0 \cos(2\theta)$, where θ is the polar angle measured from the crystallographic a axis. This PP is very different from the isotropic s-wave PP as it changes sign and has nodes for $\theta = \frac{\pi}{4} + \frac{\pi}{2}n$, where n is an integer. Thus it is expected that the properties of N/HTS contacts should differ from those of N/S contacts. Tanaka and Kashiwaya [5] have extended the BTK calculation to the case of an anisotropic PP, $\Delta(\theta)$, and have shown that the conductance curves differ from those calculated by BTK. They have defined $Z = \frac{2mH}{\hbar^2 k_F} = 2Z_{\mathrm{BTK}}$; henceforth we use this definition. For a d PP a zero bias conductance peak (ZBCP) appears for in-plane contacts reflecting the existence of Andreev surface bound states [6]. It is most pronounced for (110) contacts. For a (100) contact, the low bias dip which evolves in the case of an s-wave PP for $Z > 0$ appears only for $Z \gtrsim 0.4$ and the amplitude of the normalized conductance maxima is lowered considerably, reaching a value of around 1.5, as shown in Fig. 1(a), compared to a value of around 2.1 in the s-wave case for this Z value. Experimentally, data on Andreev reflection at low Z ($Z < 1$) contacts with HTS are limited. Results on $YBa_2Cu_3O_{7-\delta}$ (YBCO) were reported by Hass *et al.* [7] with Z values as low as 0.3 and by Yagil *et al.* [8]. Wei *et al.* [9] have reported a measurement on YBCO with a fit to a d PP. Measurements on $La_{2-x}Sr_xCuO_4$ were reported

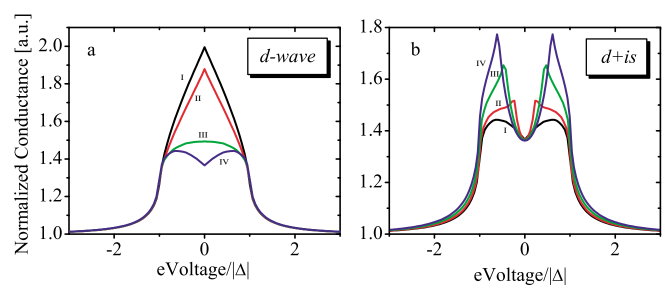

FIG. 1 (color online). Theoretical calculation ($T = 0$): normalized conductance vs normalized voltage. (a) d PP, (100) contact, $Z = 0$ (I), 0.1 (II), 0.4 (III), and 0.5 (IV). (b) $d + is$ PP, (100) contact, $Z = 0.5$, $\frac{\Delta_s}{\Delta_d} = 0$ (I), 0.25 (II), 0.5 (III), and 0.75 (IV). $|\Delta|$ is the maximum amplitude of the PP.

by Achsaf *et al.* [10] with a fit to an anisotropic s-wave PP and by Gonnelli *et al.* [11] with a fit to a $d + id_{xy}$ PP and Z values as low as 0.135.

Here we report on Andreev reflection spectroscopy measurements using a point contact between a normal metal (Au) and $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ thin films. By fitting our data to the theory of Tanaka and Kashiwya [5], we are able to find the symmetry of the PP at different barrier transparencies. Our results are best fitted to the model using a PP having the $d + is$ symmetry. The amplitude of the is component is large at low Z ($Z < 0.5$), where it reaches 80% of the d amplitude, and small at large Z. This dependence on the barrier transparency implies that the large value of the is component seen at low Z values is the result of an unusual proximity effect, which modifies the PP in the HTS near the interface with a normal metal. Our results are consistent with the small imaginary component observed by STM (as a low transparency contact) as reported by Sharoni *et al.* [12].

In this study we have used $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ sputtered thin films, with $x = 0, 0.05, 0.1$, and 0.2. The growth procedure of these films was described in Refs. [13,14]. The critical temperature of the films was determined by measuring the resistance versus temperature. X-ray diffraction was used to determine the global film orientation (Table I). Sharoni *et al.* [12], using STM topographic scans, have shown that (110) films grown under the same conditions as those we have used expose (100) facets. Scanning electron microscope and atomic force microscope pictures of the Ca doped (001) films show a-axis grains on the surface of the film. Thus, in all three film orientations (100), (110) and (001), (100) facets are exposed at the film surface. Ozawa *et al.* [15] have studied the electronic properties of the surfaces of (110) oriented YBCO films. They have found that the degradation time of (110) facets is significantly smaller than that of (100) facets. We therefore expect that in our films the chances of obtaining a good metallic contact with a (100) facet are considerably higher in comparison to a (110) facet. Our contacts were formed using a mechanically cut Au tip mounted on a differential screw. All measurements were taken at a temperature of 4.2 K.

We have analyzed the measured conductance spectra by fitting them to theoretical curves calculated using the formulas developed by Tanaka [5]. The procedure requires selection of the PP symmetry. We have tried the following possibilities: d, $d + is$, $d + id_{xy}$, and $d + s$. Within the selected symmetry the fitting algorithm has the following adjustable parameters: the amplitudes of the PP components, the barrier strength Z, the orientation of the surface in contact with the normal metal [(100), (110), etc.] and the contact's degree of directionality, namely, the width of the tunneling cone. The latter is dependent upon the barrier strength, Z. Following Wei *et al.* [9], in a high Z, tunneling contact, we would expect the width of the cone to be around 20°, while for a clean N/S contact we expect a value of almost 90°. Therefore in calculating the theoretical fitting curves, for our clean N/S contacts we have used a 90° cone. The temperature for all calculated curves was set to 4.2 K in accordance with the experimentally measured value. A lifetime broadening parameter (Dynes [16]) Γ was used to account for any smearing beyond the thermal one. We have found all our results to be best fitted using a $d + is$ symmetry and (100) orientation, adjusting only the values of Δ_d, Δ_s, Z, and Γ (see Table I). Some of the curves can be fitted also using a $d + id_{xy}$ symmetry PP; however, this requires using a narrow tunneling cone in the fit, which is unreasonable for a metallic, low barrier, contact. As for the $d + s$ PP symmetry, it requires using $\Delta_s > \Delta_d$; thus we find it less probable as it fails to explain experimental data obtained for high Z contacts [12,17] and would suggest that the s-wave channel is stronger than the d-wave one, which is in conflict with the findings of most experimental data [4].

In Fig. 2 we show three examples of our measured conductance data and the best fit curve for each of them. They are ordered by increasing contact's transparency, as determined by the Z value obtained from the best fit. The absence of a ZBCP suggests that for a d PP the data could be fitted only assuming a (100) oriented contact. Figure 2(a) shows a maxima in the normalized conductance with a value of around 1.3 which one would expect could be fitted using the d symmetry [see Fig. 1(a)]. Indeed, the best fit parameters are given by $Z = 0.68$, $\Delta = 18.6meV\cos(2\theta) + i0.8meV$, $\Gamma = 2.7meV$, and (100) orientation. In this case the additional is component needed to fit the data is very small and considering the smearing factor $\Gamma = 2.7meV$ could very well be even zero. Figure 2(b) shows two distinct features (marked by arrows in the figure): (i) a maxima at around ± 7.4 mV and (ii) a distinct change of slope at around ± 18 mV. It is impossible to reproduce this behavior for the case of a pure d PP, as it has only a single energy scale,

TABLE I. Summary of fit parameters and x-ray data.

No.	Ca	X ray[a]	T_{c_o} [b] [K]	T_{c_d} [c] [K]	Z	Δ_d [d]	Δ_s [d]	Γ [d]
1	0	(100)	91	89	0.34	20.1	16.3	0.9
2	0	(110)	86	78	0.39	13.0	10.7	0.9
3	0.05	(110)	88	77	0.40	16.3	12.0	1.7
4	0.2	(110)	76	64	0.46	15.9	8.5	1.7
5	0.1	(001)	91	82	0.49	17.1	7.2	1.8
6	0.05	(001)	90	85	0.52	25.1	0	1.4
7	0	(110)	83	63	0.53	11.4	7.2	3.2
8	0.1	(110)	91	86	0.60	19.4	0	2.1
9	0.1	(100)	79	71	0.68	16.6	0	2.8
10	0.1	(001)	85	71	0.68	18.6	0.8	2.7
11	0.05	(110)	88	77	0.70	18.1	1.3	6.1

[a](100) orientation was used in the fit for all contacts.
[b]Transition onset.
[c]Transition downset.
[d]meV.

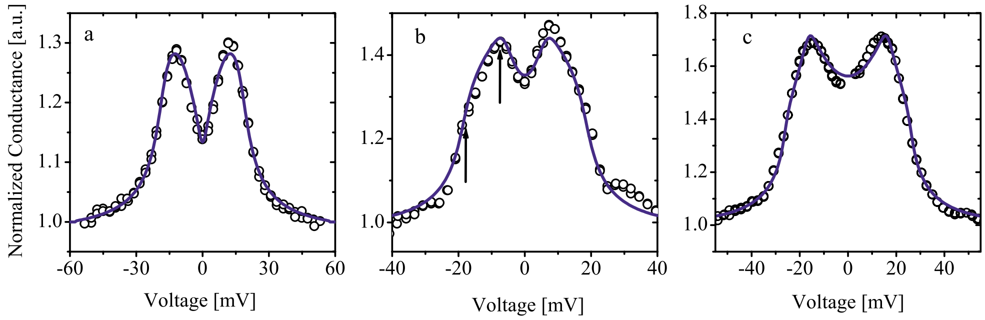

FIG. 2 (color online). Normalized conductance vs voltage: $T = 4.2$ K (circles); theoretical fit (line). (a) Sample 10: $R_N = 40\ \Omega$, $\Delta = 18.6 meV \cos(2\theta) + i0.8 meV$, $Z = 0.68$, $\Gamma = 2.7 meV$, and (100) orientation. (b) Sample 5: $R_N = 24\ \Omega$, $\Delta = 17.1 meV \cos(2\theta) + i7.2 meV$, $Z = 0.49$, $\Gamma = 1.8 meV$, and (100) orientation. Arrows point out to the manifestation of the two energy scales, maxima, and change of slope. (c) Sample 1: $R_N = 4.8\ \Omega$, $\Delta = 20.1 meV \cos(2\theta) + i16.3 meV$, $Z = 0.34$, $\Gamma = 0.9 meV$, and (100) orientation.

but we can correlate these experimental features to the values of Δ_s and $|\Delta| \equiv \sqrt{(\Delta_d)^2 + (\Delta_s)^2}$, respectively, in the case of a $d + is$ PP [see Fig. 1(b)]. For this contact, we find $Z = 0.49$, and the amplitude of the is component is enhanced. The other fit parameters are given by $\Delta = 17.1 meV \cos(2\theta) + i7.2 meV$, $\Gamma = 1.8 meV$, and (100) orientation, giving $\frac{\Delta_s}{\Delta_d} \approx 0.4$. Figure 2(c) shows the conductance curve measured on our highest transparency contact, $Z = 0.34$. The amplitude of the maxima in the normalized conductance is around 1.7. Comparing to Fig. 1(a), it obviously cannot be fitted using the pure d PP (a peak amplitude of 1.7 can be reached using $Z \approx 3$, but then the zero bias conductance would be lower than the high bias one). Using the $d + is$ PP we can reproduce the higher peak amplitude without lowering the zero bias value [see Fig. 1(b)]. We obtain a best fit using $\Delta = 20.1 meV \cos(2\theta) + i16.3 meV$, $\Gamma = 0.9 meV$, and (100) orientation. As can be judged from Fig. 1(b) the main effects of adding an is component are to increase the split between the conductance peaks and to enhance the maximum conductance. This trend is apparent in Figs. 2(a)–2(c).

In Fig. 3 we have plotted $\frac{\Delta_s}{|\Delta|}$ and $\frac{\Delta_d}{|\Delta|}$ as a function of Z. As the samples have different critical temperatures we can expect variations in the values of Δ_d and Δ_s even for a constant value of Z. To eliminate these changes we have normalized the two PP components, Δ_d and Δ_s, by dividing them by $|\Delta|$. The relative amplitude of the is component increases from values as low as (0–10)% for Z around 0.7 up to values of around 60% for Z around 0.3. At the same time the relative amplitude of the d-wave component decreases. There is no obvious correlation with the level of Ca doping or with T_c. The slope of $\frac{\Delta_s}{|\Delta|}$ as a function of Z is maximum at $Z \approx 0.5$. At low Z, the two normalized PP components appear to converge towards a value close to $1/\sqrt{2}$, i.e., $\Delta_s \approx \Delta_d$. We thus see a change from a PP which is an almost pure d wave for the high Z contacts to a PP with almost equal amplitudes of the two components in the low Z regime, the crossover between the two regimes occurring around $Z = 0.5$. In Fig. 4 we have plotted $|\Delta|$ as a function of $T_{c_{\text{downset}}}$. The data are consistent with $2|\Delta| = \eta K_B T_c$, where $\eta = 6.0 \pm 0.4$. The fact that there is some scattering in the data is to be expected as the films are never completely homogeneous. One must remember that $|\Delta|$ represents a local property of the film (at the contact), whereas T_c measures a global property.

We have shown that our data correspond to a $d + is$ symmetry PP, with the value of the imaginary component being a decreasing function of Z. A development of a subdominant imaginary PP (SIPP) near the surface of a

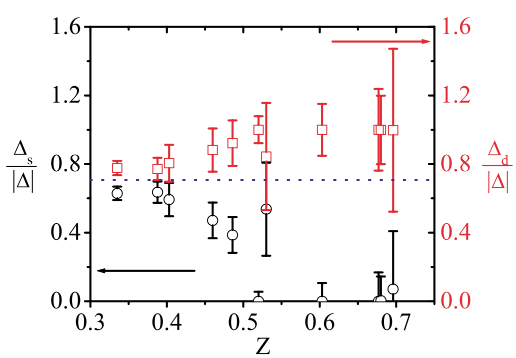

FIG. 3 (color online). The relative weight of the PP components, $\frac{\Delta_s}{|\Delta|}$ (circles) and $\frac{\Delta_d}{|\Delta|}$ (squares), as a function of the barrier strength, Z. The low Z value to which the two normalized PP components appear to converge, $1/\sqrt{2}$ (dotted line) .

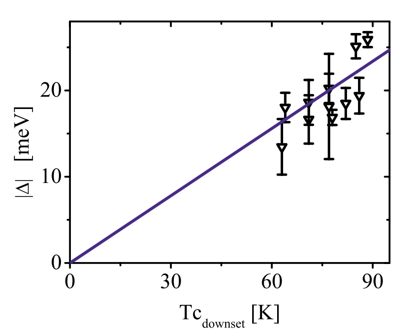

FIG. 4 (color online). Maximum amplitude of PP, $|\Delta| \equiv \sqrt{(\Delta_d)^2 + (\Delta_s)^2}$, as a function of Tc_d (triangles); see Table I.

d-wave SC was predicted theoretically by Tanuma *et al.* [18] who performed a self-consistent calculation of the spatial dependence of the PP. They did not predict any change in the PP symmetry for a (100) contact. For the case of a (110) contact in which the predicted SIPP is maximal, the lower the contact's transparency is, the stronger the reduction of the *d*-wave amplitude is, and the higher the SIPP amplitude is; i.e., the SIPP amplitude is predicted to be a decreasing function of the contact's transparency. This is inconsistent with our experimental findings. However, Tanuma *et al.* did not take into account the possibility that an induced pairing amplitude can appear in the N side, i.e., a proximity effect, and the related effect this may have on the PP in the SC in the vicinity of the interface. The proximity effect between a HTS and a normal metal was studied by Ohashi [19], who predicted that an *s*-wave symmetry pairing amplitude is induced in N by the *d* SC. According to his prediction this should lead to a reduction of the *d* amplitude towards the N/S interface on the superconducting side. This effect is maximized for a contact with the (100) face of a *d* SC and is enhanced in high transparency contacts.

We believe that our findings can be explained as a result of a proximity effect by making the following change in the proposal of Ohashi. Indeed when a normal metal is in contact with a (100) boundary of a *d*-wave SC there appears an *s*-wave symmetry pairing amplitude in the normal metal and a decrease of the *d*-wave amplitude in the HTS near the boundary. But in order to reduce the loss of condensation energy on the S side, we suggest that an *is* SIPP develops in the *d*-wave SC, in the vicinity of the barrier, in a way similar to that predicted by Tanuma *et al.* [18] for a (110) oriented contact. Considering our experimental findings, we conclude that YCaBaCuO has a subdominant *s*-wave pairing channel; otherwise the appearance of the *is* PP would have been energetically quite unfavorable. This subdominant channel exists for a broad range of Ca doping. Comparing our results to those of Gonnelli *et al.* [11], obtained on LaSrCuO, we find that though the symmetry used by Gonnelli *et al.* is a different one ($d + id_{xy}$ compared to the $d + is$) both experiments indicate that an imaginary component is added to the *d* PP. All of the spectra reported by Gonnelli *et al.* are for high transparency contacts ($Z < 0.5$); therefore no Z dependence of the two components can be inferred from their results. However, the ratio of $\Delta_{d_{xy}}/\sqrt{(\Delta_{d_{xy}})^2 + (\Delta_{d_{x^2-y^2}})^2} \approx 0.6$ that they find for doping values around the optimum level is not too far from the one we report here for the same doping levels in YCaBaCuO. It is important to point out that though we conclude that the large *is* component that we have measured for highly transparent contacts is a result of an unusual proximity effect, we do not suggest that this is the only scenario leading to the appearance of a SIPP in HTS. Various groups have measured a split in the ZBCP, explained by an appearance of a SIPP, in both planar [20,21] and STM [12] tunneling junctions with (110) orientation, where the low transparency suggests that the mechanism leading to the appearance of the SIPP is unrelated to a proximity effect. A SIPP was also found by Farber and Deutscher [22] from measurements of the temperature dependence of the penetration depth in Ca overdoped YBCO samples, where no normal metal is involved. Theoretically the appearance of a SIPP was suggested by Matsumoto and Shiba [23] and by Fogelström *et al.* [24]; however, they had calculated the case of low transparency contacts.

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