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 $d_{x^2-y^2}+i\sigma$ symmetry. We find that the amplitude of the $i\sigma$ 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) $\Delta (r)=V(r) F(r)$ where $V(r)$ is the potential representing the electron-electron interactions and $F(r)\equiv\langle\Psi_\uparrow(r)\Psi_\downarrow(r)\rangle$ 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 $F(r)$ to be zero in N and to reach a constant value in S. However near the interface $F(r)$ has a non zero 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\textsuperscript{1}. Microscopically the mechanism involved in the creation of this non zero pair amplitude $F(r)$ in the normal metal is a special reflection process known as an Andreev reflection\textsuperscript{2}, which occurs when there is an abrupt change in the PP. Such a change occurs at a clean N/S contact, where $F(r)$ is continuous, due to the difference in $V(r)$ in the two materials. An electron approaching the superconductor(SC) from the normal metal with energy smaller than $\Delta$ cannot enter as a quasiparticle into $\Delta(\theta)$ in the in-plane orientation. The conductance spectra are best fitted with a pair potential having the $d_{x^2-y^2}$ symmetry. We find that the amplitude of the $i\sigma$ 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.

For a perfectly transparent, small N/S contact, of size $a<<l$, 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.\textsuperscript{2}(BTK) 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, $Z=\frac{\mu v_p}{e}\sqrt{\pi}$, where $v_p$ is the Fermi velocity. A clean N/S contact is described by $Z=0$ and a high barrier tunnelling contact by $Z>>1$. 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 $d_{x^2-y^2}+i\sigma$ symmetry\textsuperscript{3}, described by $\Delta (k)=\Delta_0 \cos(2\theta)$, where $\theta$ 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\textsuperscript{4} 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 $Z=\frac{2mH}{e\mu v_p}=2Z_{BTK}$ henceforth we shall 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\textsuperscript{5}. It is most pronounced for (110) contacts. For a (100) contact, the low bias dip which evolves in the case of a s-wave PP for $Z>0$, appears only for $Z\gtrsim0.4$ and the amplitude of the normalized conductance maxima is lowered considerably, reaching a value of around 1.5, as shown in Fig. 1a, 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 ($Z\ll1$) contacts with HTS is limited. Results on YBCO were reported by Hess et al.\textsuperscript{6} and Yagil et al.\textsuperscript{7}. Wei et al.\textsuperscript{8} have reported a measurement on YBCO with a fit to a d PP. Measurements on $La_{2-x}Sr_xCuO_4$ were reported by Achesaf et al.\textsuperscript{9} with a fit to an anisotropic s-wave PP and by Gonnelli et al.\textsuperscript{10} with a fit to a $d+i\sigma$ PP.

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 Kashiwaya\textsuperscript{2}, 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 $d+i\sigma$ symmetry. The amplitude of the $i\sigma$ 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 $i\sigma$ 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.\textsuperscript{11}. 
The critical temperature of the films was determined using dSC. The procedure of these films were described in ref. [20, 21].

![Diagram](image)

**Fig. 1:** (color in online version) Theoretical calculation ($T=0$): normalized conductance vs normalized voltage. (a) $d$ PP, (100) contact, $Z=0$ (black), 0.1 (red), 0.4 (green), 0.5 (blue); (b) $d+s$ PP, (100) contact, $Z=0.5$, $\Delta=0$ (black), 0.25 (red), 0.5 (green), 0.75 (blue). $|\Delta|$ is the maximum amplitude of the PP.

| Table I: Summary of fit parameters and X-ray data. |
|---|
| No. | Ca | X-ray | $T_c$ | $T_{co}$ | $Z$ | $\Delta_d$ | $\Delta_s$ | $\Gamma$ |
| 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 |

*($^{(100)}$ orientation was used in the fit for all contacts

*Transition onset

*Transition downset

*meV

In this study we have used $Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$ sputtered thin films, with $x=0.0, 0.05, 0.1$ and 0.2. The growth procedure of these films were described in ref. [20, 21].

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 1). Sharoni et al. [14], using STM topographic scans have shown that (110) films grown under the same conditions as those we have used, expose (100) facets. SEM and AFM 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 4.2K.

We have analyzed the measured conductance spectra by fitting them to theoretical curves calculated using the formulas developed by Tanaka [22]. 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 tunnelling cone. The latter is dependent upon the barrier strength, $Z$. Following Wei et al. [11], in a high $Z$, tunnelling 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 4.2K in accordance with the experimentally measured value. A life-time broadening parameter (Dynes[16]) $\Gamma$ 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 $\Delta_s, \Delta_d, Z$ and $\Gamma$(see table 1). Some of the curves can be fitted also using a $d + id_{xy}$ symmetry PP, however this requires using a narrow tunnelling 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 [14, 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 [18].

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 $d$ 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 4.2K in accordance with the experimentally measured value. A life-time broadening parameter (Dynes[16]) $\Gamma$ 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 $\Delta_s, \Delta_d, Z$ and $\Gamma$(see table 1). Some of the curves can be fitted also using a $d + id_{xy}$ symmetry PP, however this requires using a narrow tunnelling 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 [14, 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 [18].

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. Fig. 2a 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. 1a). Indeed, the best fit parameters are given by $Z=0.68, \Delta = 18.6meV, cos(2\theta) = 0.8meV, \Gamma = 2.7meV$ 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. Fig. 2b shows two distinct features (marked by arrows in the figure), first a maxima at around $\pm 7.4$ mV, and second a distinct change of slope at around $\pm 18$ mV. It is impossible to reproduce this behavior for the case of a pure $d$ PP, as it has only a single energy scale, but we can correlate these experimental features to the val-
with the level of Ca doping or with component decreases. There is no obvious correlation
At the same time the relative amplitude of the d-wave component increases from values as low as 0-10% for Z
the maximum conductance. This trend is apparent in the split between the conductance peaks and to enhance
orientation, giving \( \Delta = 17 \) 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, \( R_N = 4.8 \Omega, \Delta = 17 \) meV, \( Z = 0.7 \) up to values of around 60% for Z around 0.3.

\[ \Delta = 17 \text{ meV} \cos(2\theta) + i16.3 \text{ meV}, Z = 0.34, \Gamma = 0.9 \text{ meV} \] and (100) orientation.

The main effects of adding an component is enhanced. The other fit parameters are given by \( \Delta = 17.1 \text{ meV} \cos(2\theta) + i7.2 \text{ meV}, \Gamma = 1.8 \text{ meV} \), and (100) orientation, giving \( \frac{\Delta_\theta}{\Delta} \approx 0.4 \). Fig. 2c 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. 1a, it obviously can not 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. 1b). We obtain a best fit using \( \Delta = 20.1 \text{ meV} \cos(2\theta) + i16.3 \text{ meV}, \Gamma = 0.9 \text{ meV} \), and (100) orientation. As can be judged from Fig. 1b 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 Fig. 2a through Fig. 2c.

In Fig. 3 we have plotted \( \frac{\Delta_\theta}{\Delta} \) and \( \frac{\Delta_\theta}{\Delta} \) as a function of Z. As the samples have different critical temperatures we can expect variations in the values of \( \Delta_\theta \) and \( \Delta_\theta \) even for a constant value of Z. To eliminate these changes we have normalized the two PP components, \( \Delta_\theta \) and \( \Delta_\theta \), 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 \( \frac{\Delta_\theta}{\sqrt{2}} \) 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 \( \frac{\Delta_\theta}{\sqrt{2}} \), i.e. \( \Delta_\theta \approx \Delta_\theta \). 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 \( T_{cdownset} \). The data is 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

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

![FIG. 3: The relative weight of the PP components, \( \frac{\Delta_\theta}{\Delta} \) (circles) and \( \frac{\Delta_\theta}{\Delta} \) (squares) as a function of the barrier strength, Z. The low Z value to which the two normalized PP components appear to converge. \( \frac{\Delta_\theta}{\sqrt{2}} \) (dotted line)](image)

![FIG. 4: Maximum amplitude of PP, \( |\Delta| = \sqrt{(\Delta_\theta)^2 + (\Delta_\theta)^2} \) as a function of \( T_{cdownset} \) (triangles)](image)
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 corresponds 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 d-wave SC was predicted theoretically by Tanuma et al.\[12] 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 is the contact’s transparency, the stronger is the reduction of the d-wave amplitude and the higher is the SIPP amplitude, 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 Y. Ohashi\[8] for a (110) oriented contact. 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 Y. Ohashi. Indeed when a normal metal is in contact with a (100) boundary of a d-wave SC there appears a $s$-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 a 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.\[12] 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 $s$ 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.\[13], obtained on LaSrCuO, we find that 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 $\frac{\Delta_{d_{xy}}}{\sqrt{(\Delta_{d_{xy}})^2+(\Delta_{d_{2-x-y}})^2}} \approx 0.6$ 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\[19, 22] and STM\[14] tunnelling 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 Faber and Deutscher\[23] from measurements of the temperature dependence of the penetration depth in Ca over-doped YBCO samples, where no normal metal is involved.

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