Evidence of a d- to s-Wave Pairing Symmetry Transition in the Electron-Doped Cuprate Superconductor $Pr_{2-x}Ce_xCuO_4$

Amlan Biswas,[1] P. Fournier,[2] M. M. Qazilbash,[1] V. N. Smolyaninova,[1] Hamza Balci,[1] and R. L. Greene[1]

[1]*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742*
[2]*Centre de Recherche sur les Propriétés électroniques de matériaux avancés, Département de Physique, Université de Sherbrooke, Québec, Canada J1K 2R1*

We present point contact spectroscopy (PCS) data for junctions between a normal metal and the electron-doped cuprate superconductor $Pr_{2-x}Ce_xCuO_4$ (PCCO). For the underdoped compositions of this cuprate ($x \sim 0.13$) we observe a peak in the conductance-voltage characteristics of the point contact junctions. The shape and magnitude of this peak suggest the presence of Andreev bound states at the surface of underdoped PCCO which is evidence for a d-wave pairing symmetry. For overdoped PCCO ($x \sim 0.17$) the PCS data do not show any evidence of Andreev bound states at the surface suggesting an s-wave pairing symmetry.

The symmetry of the superconducting order parameter is a crucial input for theories on the mechanism of superconductivity in cuprates. It is now generally believed that the hole-doped high-T_c cuprates have a d-wave pairing symmetry [1,2]. However, for the electron-doped (n-doped) cuprates $R_{2-x}Ce_xCuO_4$ ($R = Nd$, Pr, Sm, or Eu) the situation is still not entirely clear. Initially it was believed that these compounds have an s-wave symmetry from measurements of penetration depth in $Nd_{2-x}Ce_xCuO_4$ [3–5]. In addition, tunneling spectroscopy experiments showed no evidence of a zero bias conductance peak (ZBCP) [which is caused by Andreev bound states (ABS) in a d-wave superconducting system], another indication of s-wave symmetry [6]. However, Cooper [7] suggested that the paramagnetic moment of the Nd^{3+} ions could mask the power law dependence of $\lambda(T)$ that is the indication of nodes in the order parameter. Consistent with this argument, recent penetration depth measurements in $Pr_{2-x}Ce_xCuO_4$ (PCCO) have shown clear evidence of nodal quasiparticles [8,9]. Strong evidence of d-wave pairing symmetry was also provided by Tsuei *et al.* [10], who observed a trapped half-flux quantum at a tricrystal grain boundary junction, and by recent photoemission experiments [11]. However, the issue has not been completely resolved. Two other penetration depth measurements on PCCO have given evidence of s-wave pairing symmetry [12,13], and alternative explanations for the available data have also been suggested [14]. Moreover, there has still been no convincing evidence of a ZBCP in the tunneling spectra of n-doped cuprates [13]. Two recent reports on $Nd_{2-x}Ce_xCuO_4$ did show a ZBCP [15,16]. However, the conditions under which the ZBCP appeared were ambiguous [15], and the appearance of the ZBCP was not attributed to d-wave symmetry [16].

In the case of the hole-doped cuprate $YBa_2Cu_3O_{7-\delta}$ (YBCO), recent reports have shown evidence of a transition from a pure $d_{x^2-y^2}$ pairing symmetry in underdoped compositions to a $d + id_{xy}$ pairing symmetry in overdoped compositions [17]. This transition occurs across

a quantum critical point (QCP) near optimal doping. In fact, recent penetration depth measurements on n-doped cuprates also show evidence of a transition from a d-wave symmetry for underdoped compositions to an s-wave symmetry for the overdoped region [18]. In this paper we present point contact spectroscopy (PCS) data on the electron-doped high-T_c cuprate superconductor PCCO for the underdoped and overdoped compositions. Our data show that underdoped PCCO has a d-wave pairing symmetry and overdoped PCCO has an s-wave pairing symmetry.

Blonder *et al.* [19] have discussed the current-voltage (I-V) characteristics of an s-wave superconductor-normal metal junction separated by a barrier of arbitrary strength. The barrier strength is parametrized by a dimensionless number Z such that a direct contact between a normal metal and a superconductor corresponds to $Z = 0$, while for the tunneling limit $Z \gg 1$. The calculated $G/G_N - V$ curves ($G \equiv dI/dV$ and G_N is the value of G well outside the gap region) for different Z are shown in Fig. 1a. Kashiwaya *et al.* [20,21] have dealt with the same problem for an anisotropic d-wave superconductor. The calculated curves for tunneling into the (110) planes are summarized
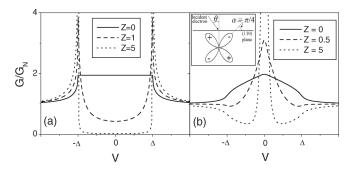

FIG. 1. (a) Calculated G-V curves for an s-wave superconductor at zero temperature using the BTK model. (b) Calculated G-V curves for a d-wave superconductor at zero temperature for current going into the (110) plane (inset).

in Fig. 1b. The inset shows tunneling in the (110) plane and defines angles θ and α, which will be used later. Note that even for $Z > 0$ there is a peak at zero bias in contrast to the s-wave case. This ZBCP is formed due to surface ABS and is one of the unique features of a d-wave superconductor [22] and has been consistently observed in YBCO [23–25]. For $Z > 0$ the ZBCP is formed for all directions in the a-b plane except when tunneling into the (100) and (010) planes [20,21]. The difference in the I-V characteristics for the s- and d-wave cases at low Z will form the basis of our experiments. PCS is a powerful technique for making such low Z junctions [26].

In this Letter we discuss our a-b plane PCS data on thin films of PCCO. Films of thickness 2500 Å were grown using pulsed laser deposition on LaAlO$_3$ and yttria stabilized zirconia substrates. Details of the film growth are given in Ref. [27]. The films have been optimized for oxygen content by maximizing T_c for each cerium concentration. The films were characterized by x-ray, ac susceptibility, and resistivity measurements. The first obstacle in carrying out experiments in the same configuration as the ones on YBCO [23,25] is that (110)-oriented thin films of PCCO have not been grown. Instead, we have used c-axis oriented thin films to form a-b plane junctions by making a point contact on the side of the film as described in Ref. [28]. A film of PCCO is cleaved and a gold tip [29] is pressed immediately on the side to form a PCCO/Au point contact. This ensures that the current flow is perpendicular to the c axis and the junction roughness leads to contributions from different directions in the a-b plane. The data obtained did not show any qualitative change when the cleavage direction was varied. The G-V curves were obtained using a standard lock-in technique.

In point contact junctions the Z is reduced by increasing the pressure of the point contact which also results in a decrease of the junction resistance [30]. The G-V curves for such a low Z junction on a thin film of underdoped PCCO ($x = 0.13$) at $T = 1.6$ K is shown in Fig. 2. The T_c of this particular film is 12.2 K. Without any further analysis we can see that $G_0/G_N \approx 3$. Both the shape and magnitude of this peak in the G-V curve strongly suggests a d-wave pairing symmetry. A ratio of G_0/G_N greater than 2 is inconsistent with an s-wave symmetry. As shown in Fig. 1a for $Z = 0$, G_0/G_N reaches a maximum value of 2 for $-\Delta_{SC} < V < \Delta_{SC}$ [19]. For a d-wave superconductor the value of G_0/G_N can have a value greater than 2 due to the ABS at the surface as shown in Fig. 1b [20,21] and shown experimentally for YBCO in Ref. [31]. Therefore, this peak we observe is a manifestation of the ABS formed at the surface due to the d-wave pairing symmetry of underdoped PCCO ($x = 0.13$). The inset (b) of Fig. 2 shows a comparison of our data with a theoretical curve calculated using the method of Ref. [20]. The parameters for the theoretical curve are $Z = 1.2$, Δ_{SC} (for an anisotropic gap this is the maximum gap value) $= 7$ meV, and $\alpha = \pi/6$ [$\alpha = \pi/4$ implies current perpendicular to
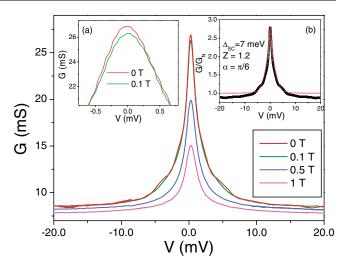

FIG. 2 (color). G-V characteristics for a low Z, a-b plane point contact junction between a thin film of PCCO ($x = 0.13$) and gold at $T = 1.6$ K. The G_0/G_N ratio is ~ 3.0. For a magnetic field of 1000 G there is a very small suppression of the peak [inset (a)]. Larger fields reduce the width and the height of the peak. A comparison with a calculated curve for a d-wave pairing symmetry (red line) is shown in inset (b).

the (110) planes; see inset of Fig. 1b]. For these low Z junctions the angular integral was taken over the full range of $-\pi/2 < \theta < \pi/2$. This calculation shows a good quantitative match with our data and is strong evidence of the d-wave pairing symmetry in underdoped PCCO. It should be mentioned here that the calculated curve is the simplest form of the theory. Additional effects are introduced due to Fermi velocity mismatch between Au and PCCO, which modifies Z and makes it angle dependent [32], and due to surface roughness. The angle dependence of Z will modify the limits of θ and hence the tunneling cone (range of angles of the incident electrons contributing to the current transport). Surface roughness leads to different facets being exposed at the junction, and there is not just a single value but a range of α. While these factors will affect the parameters which we have used for the calculated spectrum in Fig. 2, the conclusion that this spectrum is due to the d-wave pairing symmetry is still valid.

We have shown above that due to the d-wave pairing symmetry of underdoped PCCO, ABS are formed on the surface which is reflected in the observed point contact spectra. In tunnel junctions on YBCO, a ZBCP is observed in the tunneling spectra due to the surface ABS, and this ZBCP splits when a magnetic field is applied perpendicular to the a-b plane [23,25]. Figure 2 shows that a magnetic field applied perpendicular to the a-b plane just results in a reduction of both the height and the width of the peak but does not result in an observable splitting of the peak. The inset (a) of Fig. 2 shows the effect of a small field of 1000 G. A very slight reduction of the height is seen. Why do we not see a field induced splitting in our junctions if the peak is formed due to ABS? One mechanism for the splitting of the ZBCP in YBCO is related to Meissner

screening currents [23,33]. At low fields the splitting, δ, increases linearly with the applied field H. However, the screening currents saturate at the pair breaking critical field $H_c = \phi_0/\pi^2 \xi \lambda$ [33] where ϕ_0 is the flux quantum. The value of H_c for optimally doped PCCO is about 1000 G at $T = 1.6$ K, taking the coherence length $\xi \sim 60$ Å [34] and the penetration depth λ about 2500 Å [9]. This makes the linear part of the δ-H curve very small and the splitting cannot be resolved at the temperatures of our experiments. Another possible origin of the field splitting of the ZBCP in YBCO is a field induced subdominant gap symmetry of the form id_{xy} [35]. So the absence of the field splitting in the PCCO case could be due to a different (e.g., is) or nonexistent subdominant gap symmetry in underdoped PCCO. Experiments at subkelvin temperatures will be necessary to resolve the field splitting issue.

So far we have discussed data for underdoped PCCO ($x = 0.13$) which shows the d-wave nature of the pairing symmetry in that doping range. What happens at higher doping values? Figure 3 shows a G-V curve for a low Z junction on a thin film of overdoped PCCO ($x = 0.17$) at $T = 1.58$ K. The T_c for this particular film is 11.8 K. The results are strikingly different from the underdoped case. The most important feature is the dip in G_0/G_N at zero bias. This dip shows that there are no ABS at the surface of overdoped PCCO. According to the discussion above, overdoped PCCO then has an s-wave pairing symmetry. Figure 3 also shows a fit to the data using a modified Blonder-Tinkham-Klapwijk calculation with parameters $\Delta_{SC} = 1.76$ meV, $Z = 0.6$, and a lifetime broadening factor $\Gamma = 0.16\Delta_{SC}$. The significance of the small value of Δ_{SC} will be discussed later. The good fit is strong evidence that overdoped PCCO has an s-wave pairing symmetry. Such a transition from d- to s-wave symmetry across optimal doping has also been suggested by recent
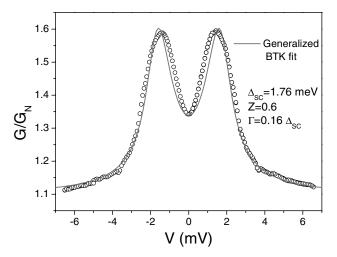
penetration depth measurements on PCCO [18]. Such doping dependent pairing symmetry has also been observed in hole-doped cuprates. Recently, a transition from a $d_{x^2-y^2}$ to a possible $d + id_{xy}$ pairing symmetry has been reported in YBCO [17], and in overdoped Ca-YBCO an s-wave component was observed [36]. A transition from a d-wave pairing symmetry in underdoped PCCO to an s-wave pairing symmetry in overdoped PCCO suggests the existence of a QCP near optimal doping. It has been shown that across a QCP for a $d_{x^2-y^2}$ superconductor only transitions to $d + id_{xy}$ or $d + is$ are stable [37]. Since our PCS data show that there are no ABS formed on the surface of overdoped PCCO and fit well to an s-wave model, it supports a transition from $d_{x^2-y^2}$ to a $d + is$ pairing symmetry with a significant s-wave component, as the doping is increased above the optimal value.

As mentioned above, for YBCO the d-wave pairing symmetry leads to a formation of a ZBCP in the tunneling limit ($Z \gg 1$) [23,25]. What happens in point contact junctions with higher Z on PCCO? The data from the higher resistance (and hence higher Z) junctions are shown in Fig. 4. Although the junction resistance is only about twice that of the junction in Fig. 2, the G-V curves are markedly different from those in Fig. 2. The superconducting gap Δ_{SC} is clearly seen and is marked in the figure. The value of Δ_{SC} from the figure is ~ 6.5 meV for the underdoped composition. Just as in earlier tunneling spectroscopy experiments, there is no hint of a ZBCP. In an earlier paper we showed that even for high-Z junctions on optimally doped PCCO, no ZBCP is observed [28]. How can we explain this if underdoped PCCO has a d-wave symmetry? There are two possible reasons. One is the effect of disorder and the other is thermal smearing. It has been shown in the case of YBCO that the ZBCP is
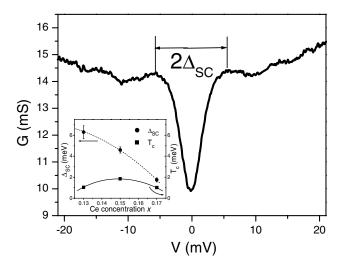
FIG. 3. G-V characteristics for a low Z, a-b plane point contact junction between a thin film of PCCO ($x = 0.17$) and gold at $T = 1.58$ K. The dip at zero bias shows the absence of Andreev bound states and suggests an s-wave pairing symmetry. The red line is a fit using a modified BTK model.

FIG. 4. G-V curve for an a-b plane point contact junction between a PCCO thin film ($x = 0.13$) and gold. This junction has a higher Z than the one in Fig. 2. No ZBCP is observed. Δ_{SC} is indicated. The inset shows the variation of Δ_{SC} and T_c with Ce concentration.

suppressed by an increase of disorder in the material [38]. The properties of n-doped cuprates are very sensitive to oxygen concentration, and it is possible that oxygen disorder at the surface suppresses the ZBCP. Also, the thermal smearing of the tunneling spectra at a temperature of 1.6 K is $\sim 5k_BT \sim 0.7$ meV. This is comparable to the expected width of the ZBCP since, from the theoretical curves in Refs. [20,21], it is clear that the width of the ZBCP scales with the value of Δ_{SC} if the Z for the junction is the same. This implies that for tunnel junctions on n-doped cuprates with a $\Delta_{SC} \approx 4$–6 meV, the width of the ZBCP (if present) should be about 1 meV.

The inset of Fig. 4a shows the variation of Δ_{SC}, estimated from the point contact spectra, with the Ce concentration x. The data for $x = 0.15$, i.e., the optimally doped composition, is taken from Ref. [28]. The variation of T_c (in meV) is also shown. Δ_{SC} decreases monotonically with increasing x. For the underdoped ($x = 0.13$) sample, $2\Delta_{SC}/k_BT_c \sim 12.4$, and it drops to about 3.4 for the overdoped ($x = 0.17$) sample which is close to the weak coupling value. Such a drop in the superconducting gap in the overdoped regime has been observed earlier for hole-doped cuprates like $Bi_2Sr_2CaCu_2O_{8+\delta}$ [39]. This is the first such observation for electron-doped cuprates.

In conclusion, we have presented the first systematic study of the formation of ABS at the surface of n-doped cuprate superconductors using point contact spectroscopy. A broad peak is observed at zero bias in the G-V curves of the low Z point contact junctions on underdoped PCCO, the shape and magnitude of which is evidence of the presence of ABS. The observation of ABS is strong confirmation of a d-wave pairing symmetry in underdoped PCCO. However, for overdoped PCCO ($x = 0.17$) we do not find evidence for ABS. Instead, the G-V curves show evidence of an s-wave pairing symmetry. This transition from d- to s-wave symmetry suggests that there is a quantum critical point near optimal doping in n-doped cuprates. Such a transition could also be the reason for the controversial results from previous experiments probing the pairing symmetry of PCCO, e.g., penetration depth measurements. Further experiments, e.g., the tricrystal grain boundary junction experiment, will have to be done over this doping range to confirm our observations.

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[29] The tip is made of beryllium-copper coated with gold. Such a tip was used since a pure gold tip was soft and the high pressures required to form low Z junctions could not be applied. The G-V curves for $T > T_c$ are featureless for the energy range shown here, which confirms that the density of states of the tip does not introduce features in the G-V curves (Ref. [28]).

[30] For underdoped films, junction resistance $R_0 \sim 120$ Ω, normal state resistivity at 1.6 K is ~ 500 $\mu\Omega$ cm, and mean free path $l \sim 6$ Å [P. Fournier *et al.,* Phys. Rev. Lett. **81**, 4720 (1998)]. From the Sharvin formalism $R_0 = 4\rho l/3\pi a^2$ where a is the contact radius, we get $a \sim 30$ Å. Hence, we are not in the ballistic limit. This leads to an increase in the effective value of Z [I. I. Mazin *et al.,* J. Appl. Phys. **89**, 7576 (2001)]. A similar argument follows for the overdoped films where $R_0 \sim 2$ Ω, $l \sim 70$ Å, $\rho \sim 40$ $\mu\Omega$ cm, and $a \sim 200$ Å.

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