Andreev Spectroscopy Study of Multigap Pairing in PrOs$_4$Sb$_{12}$

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Experimental studies of the skutterudite superconductor PrOs$_4$Sb$_{12}$ have reported various field-vs-temperature phase diagrams, with mixed evidence for nodes in the pairing gap. Some experiments have also indicated the presence of multiple gaps, suggesting that the pairing involves either multiple bands or multiple order parameters. To examine these issues, we have used Andreev reflection spectroscopy, performed with ballistic point contacts over a range of temperatures and magnetic fields. We observed distinct spectral evidence for gap nodes. We also observed multiple spectral features arising from Ru-doping. We interpret the evolution of these spectral features within the scenario of multigap pairing.

1. Introduction

The discovery of superconductivity in the heavy-fermion filled skutterudite compound PrOs$_4$Sb$_{12}$ has attracted much interest, particularly because of the its unconventional properties. A double superconducting transition at $T_{c1}$ $\sim$ 1.8 K and $T_{c2}$ $\sim$ 1.7 K has been observed$^{2-4}$ suggesting that there may be multiple superconducting phases. Different experiments have reported different field-vs-temperature ($H$ $-$ $T$) phase diagrams. For example, angular magneto-thermal-conductivity $\kappa(H, \phi)$ data indicates that a superconducting order parameter (OP) undergoes a field-induced phase transition from two point nodes at low fields, to six point nodes at high fields.$^5$ However, specific heat$^6-8$ and ac magnetic susceptibility $\chi$ measurements$^7$ have not observed this transition.

Despite numerous experimental and theoretical studies, the superconducting gap topology of PrOs$_4$Sb$_{12}$ has still not been established. Penetration depth,$^9$ $\kappa(H, \phi),$ small angle neutron scattering$^{10}$ and specific heat $C(T)$$^{11}$ experiments have all indicated the presence of gap nodes. In contrast, muon-spin resonance,$^{12}$ Sb-nuclear quadrupolar resonance,$^{13}$ scanning tunnelling spectroscopy$^{14}$ and $\kappa(T, H)$$^{15}$ measurements have shown the Fermi surface to be fully gapped in the superconducting state. PrOs$_4$Sb$_{12}$ has a complex Fermi topology with multiple sheets on the Fermi surface, and recent $\kappa(T, H)$ measurements have indicated that it is a multiband superconductor.$^{15}$ The discrepancy between experiments that see gap nodes and those that do not, can be explained by a scenario where a nodal gap exists on the small-mass band and the large-mass band is fully gapped.$^{16}$ Recent $C(T)$ measurements on Pr(Os$_{1-x}$Ru$_{x}$)$_4$Sb$_{12}$ showing fully gapped behaviour for $x$ as low as 0.01 would be consistent with this picture.$^{17}$ However, direct evidence for co-existing gaps with different symmetries is still lacking.

Point-contact spectroscopy (PCS) is a powerful technique for studying unconventional superconductors, as it is a microscopic probe of both the amplitude and phase of the OP. It has been used to reveal evidence for multiband superconductivity in MgB$_2$$^{18}$ and CeCoIn$_5$$^{19}$ Andreev reflection (AR) and quasiparticle tunnelling are the two main processes responsible for the conductance $dI/dV$ spectrum seen in a normal-metal/superconductor junction. For conventional s-wave superconductors the primary contribution to the $dI/dV$ in high transparency junctions is AR, the process by which a normal current is converted to a supercurrent.$^{20}$ These Andreev bulk states cause a hump-like feature in the $dI/dV$ spectrum resulting in excess spectral area. For superconductors with gap nodes, due to a sign change in the OP at the node, constructive interference between consecutively reflected quasi-particles results in Andreev surface states. These surface states manifest themselves in the $dI/dV$ spectrum as a peak at zero-bias accompanied by dips at higher energy.$^{21-23}$ The area of the dips and peak are equal thus conserving total spectral area.

2. Experimental

Andreev Spectroscopy measurements were made using etched Pt-Ir tips to form ballistic$^{24}$ point contacts on the c-axis faces of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ crystals for $x = 0$ and $x = 0.02$. For low Ru-doping, the effective electron mass remains enhanced$^{25}$ and Andreev spectroscopy is ideally suited to examine if a gapped OP component develops at such doping levels. The measurements were made in a $^3$He-$^4$He dilution refrigerator, down to 80 mK and up to 2.5 T. The applied magnetic field was oriented perpendicular to the c-axis faces of the crystals. Junction impedances were typically $\sim$0.2 - 1 $\Omega$. Current versus voltage ($I$-$V$) curves were obtained by current biasing the sample using a 4-lead configuration. To minimize Joule heating a pulsed technique was employed. Pulse lengths of 2 ms with a 20% duty cycle were used and the voltage was measured 80 times during each pulse and averaged. The resulting $I$-$V$ curves were numerically differentiated to obtain the $dI/dV$ spectra as a function of $V$.

Single crystal samples of Pr(Os$_{1-x}$Ru$_x$)$_4$Sb$_{12}$ were grown with a molten-metal-flux method.$^{26}$ Before measurements, to remove any excess Sb flux, the samples were etched in a 1:1 HNO$_3$-HCl mixture and rinsed in...
ethanol. Samples etched in this way showed the most reproducible spectra. Electrical resistivity \(\rho(T, H)\) was measured with an AC resistance bridge using ultra-low current modulation. For the \(x = 0\) sample a sharp superconducting transition at \(T_c \sim 1.87\,\text{K}\) was observed in zero field and at base temperature it was found that the upper critical field \(H_{c2} \sim 2.25\,\text{T}\). \(\chi(T)\) measurements were also performed for the \(x = 0\) sample and showed a double superconducting transition at \(T_{c1} \sim 1.85\,\text{K}\) and \(T_{c2} \sim 1.7\,\text{K}\).

3. Discussion

Figure 1 shows the temperature evolution of point-contact \(dI/dV\) data taken on a \(x = 0\) sample in zero magnetic field. At 90 mK there is a pronounced zero-bias conductance peak (ZBCP) accompanied by symmetric dips located at \(\sim \pm 0.4\,\text{mV}\). There are also additional satellite features at \(\sim \pm 0.3\,\text{mV}\) and \(\sim \pm 0.2\,\text{mV}\). As the temperature is increased the dips and satellite features move inward and the height of the ZBCP decreases. The \(dI/dV\) flattens out above \(T \sim 1.8\,\text{K}\). Shown in the inset is the excess spectral area, which was calculated by subtracting the normal-state conductance from each spectrum and then numerically integrating between \(\pm 1.8\,\text{mV}\). As the temperature is lowered, the excess spectral area increases.

The presence of the ZBCP provides spectroscopic evidence for nodes in the superconducting OP. Recent theoretical work has calculated the \(dI/dV\) spectra for various spin singlet and spin triplet OP's proposed for \(\text{PrOs}_4\text{Sb}_{12}\)\textsuperscript{27} The \(dI/dV\) for one of the candidate spin triplet pair potentials with point nodes shows a ZBCP and satellite features resembling those seen in Figure 1.

Figure 2 shows the temperature evolution of the \(dI/dV\) spectrum for a \(x = 0.02\) sample. At 90 mK there is a ZBCP, but its height is smaller than the one seen in the \(x = 0\) sample. Additional broad hump-like features are also observed at \(\sim \pm 0.6\,\text{mV}\) and \(\sim \pm 1.4\,\text{mV}\). As the temperature is increased both of these features become less broad and the ZBCP height decreases, eventually disappearing at \(T \sim 1.8\,\text{K}\). Shown in the inset is the temperature dependence of the excess spectral area (arbitrary units) with temperature.

Figure 3 shows the magnetic field evolution of the \(dI/dV\) spectrum for a \(x = 0\) sample at base temperature. As the field is increased the ZBCP height decreases and the dips and satellite features move inward. The ZBCP peak vanishes at \(\sim 1.5\,\text{T}\), which is lower than \(H_{c2} \sim 2.25\,\text{T}\), as determined by \(\rho(T, H)\). The inset shows the magnetic field evolution of the excess spectral area. As the field is lowered the excess spectral area increases.

Figure 4 shows the magnetic field evolution of the \(dI/dV\) spectrum for a \(x = 0.02\) sample at 80 mK. The hump-like features become less broad and the ZBCP height decreases, eventually disappearing at \(T \sim 1.8\,\text{K}\). Shown in the inset is the temperature dependence of the excess spectral area (arbitrary units).
Our spectroscopic results, (states, this temperature evolves, it is). H and surface T2.2 T. Shown in the inset is the field evolution of the excess spectral area (arbitrary units).

Ru-doping appears to have a pronounced effect on the dI/dV spectrum. For x = 0, a large ZBCP indicates that Andreev surface states are mainly contributing to the dI/dV. For x = 0.02, the emergence of broad hump-like features in the dI/dV suggest that at this doping level Andreev bulk states play a much larger role in the dI/dV spectrum compared to x = 0. Our results are qualitatively consistent with C(T) measurements which show a fully gapped OP component for doping as low as x = 0.01.11

It is worth noting that, for x = 0, the excess spectral area increases as the temperature is lowered below Tc. Andreev surface states by themselves cannot account for this excess as they should be conserved. Since excess area arise from Andreev bulk states, this temperature evolution indicates that an OP component in addition to the one responsible for the ZBCP contributes to the dI/dV. Our results therefore provide spectroscopic evidence for multiple OP components existing in PrOsSb12.

Two separate κ(T, H) studies have indicated that PrOsSb12 is a multiband superconductor.15,28 However, one of these studies suggested that the superconducting OP is fully gapped on both bands,15 whereas the other indicated that while one OP component is fully gapped (large-mass band) the other OP component is nodal (small-mass band).28 Our spectroscopic results, which also indicate the presence of a nodal OP component, are consistent with the multiband and multi-symmetry scenario proposed in Ref [28].

The spectral evolution of the x = 0 case is also remarkable. On applying a magnetic field, the excess spectral area decreases. Above 1.5 T the ZBCP is no longer visible in the dI/dV yet excess states persist to ~ 2.2 T, suggesting that in this field range only one OP component is contributing to the dI/dV. Our results are qualitatively similar with κ(H, φ) measurements which reported a field-induced change in the superconducting OP.5

The magnetic field levels above which the ZBCP is no longer discernible and up to which the excess spectral area persists has been tracked as a function of temperature. Figure 5 shows the resulting H – T phase diagram. Defining H* as the field at which the ZBCP vanishes, it can be seen that Hc2(T), as determined by ρ(T, H), and H*(T) emerge from distinct low-temperature asymptotes and appear to gradually approach each other as temperature is increased. Defining H′ as the field up to which excess spectral area persists (indicated by squares in Figure 5) it can be seen that the H′(T) and Hc2(T) points coincide. Above Hc2 the sample is no longer superconducting and so the amplitude of all OP components is zero. As the H′(T) and Hc2(T) curves overlap each other, it indicates that the OP component responsible for the excess states in the dI/dV persists up to Hc2. The behaviour of H′(T) should be contrasted with that of the OP component responsible for the ZBCP which appears to only persist up to H*.

Between H*(T) and Hc2(T) the dI/dV spectra should reflect the OP symmetry. Theoretical dI/dV spectra have been calculated for various high-temperature OPs proposed for PrOsSb12, and some of these spectra show virtually no dependence on bias voltage,27 consistent with our data above the H* curve. While it is difficult to determine the exact OP symmetry in this high-field region, from the excess spectral area observed, we can nonetheless infer that an OP component persists up to Hc2.

H*(T) and Hc2(T) appear to converge to different temperatures at H = 0 T. Since a double superconducting transition for the x = 0 sample was seen in χ(T) it is interesting to consider whether Hc2(T) converges to Tc1 ~ 1.85 K and H*(T) converges to Tc2 ~ 1.7 K. Due to the close proximity of Tc1 and Tc2, however, it is diffi-

![Fig. 4. Magnetic field dependence of conductance spectrum for a Pt-Ir/Pr(Os0.98Ru0.02)4Sb12 point-contact junction at 80 mK. Decreasing zero-bias conductance peak height corresponds to increasing field. Shown in the inset is the field evolution of the excess spectral area (arbitrary units).](image)

![Fig. 5. H – T phase diagram as determined from resistivity and point-contact spectroscopy measurements. Hc2 (diamonds) corresponds to ρ(T, H) data. H* (triangles) corresponds to the field at which the ZBCP vanishes and H′ (squares) corresponds to the field above which no excess spectral area exists. Dashed lines are a guide to the eye.](image)
cult to definitively determine whether or not the $H^*(T)$ and $H_{c2}(T)$ curves do indeed terminate at different $T_c$. Furthermore, it has not been resolved whether the double superconducting transition is intrinsic. $\kappa(T, H)$ has shown evidence for multiband superconductivity in samples exhibiting a single $T_c$. It would be interesting to spectroscopically track $H^*(T)$ and $H_{c2}(T)$ in such single $T_c$ samples and compare the low-temperature and low-field asymptotics with those observed for samples exhibiting a double $T_c$.

Ru-doping has a dramatic effect on the superconducting OP in Pr$_{1-x}$Ru$_x$Sb$_2$. Our data indicates that for $x = 0$ there are multiple OP components, one of which is nodal. The fully Ru-doped compound PrRu$_4$Sb$_{12}$ on the other hand has been reported as having a fully gapped superconducting OP. As Andreev spectroscopy is a phase sensitive local probe, it is ideally suited to examine how the OP evolves from $x = 0$ to $x = 1$. The effect of Ru-doping on the two OP-components observed in PrOs$_4$Sb$_{12}$ can be determined by obtaining a $H - T$ phase diagram at various doping levels and observing how the nodal OP component ($H^+$) is suppressed as doping is increased.

4. Conclusions

Point-contact spectroscopy measurements were performed on Pr$_{1-x}$Ru$_x$Sb$_{12}$ crystals for $x = 0$ and $x = 0.02$. For $x = 0$ a pronounced ZBCP was observed in the $dI/dV$ indicating the presence of a nodal OP component. For $x = 0.02$ additional hump-like features were seen in the $dI/dV$ below $T_c$. Excess spectral area was observed at low temperatures for both $x = 0$ and $x = 0.02$, consistent with the presence of multiple OP components with different symmetries.

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